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## ABSTRACT

This Final Technical Report for the period from 1 December 1993 to 30 November 1997 presents a summary of research performed on two classes of materials prepared by the sol-gel method. The first class of materials is the Ormosils. Work has been carried out on the structure and mechanical properties of Ormosils and a model was presented to account for the dependence of properties on structures, especially for the rubbery Ormosils. The high-temperature stability of rubbery Ormosils was found to be enhanced by the presence of small amounts of iron ions. A method was developed for the introduction of carbon black into Ormosils. Aerogels of 95% porosity were known to be extremely fragile. By the incorporation of polydimethyl siloxane, the resultant Ormosils were rendered rubbery. The second family of materials investigated consisted of ferroelectric thin films. Single crystals of  $\text{KNbO}_3$  films were grown by the sol-gel method, etched to form waveguides and shown to emit green light when impinged upon by infrared lasers due to second harmonic effects. A theory was postulated which enabled the understanding of ferroelectric behavior shown by amorphous oxide films. A technique was developed for the successful growth of multilayered stack of alternating oxide films. A new family of organic-inorganic hybrids which showed ferroelectric behavior was discovered by the incorporation of an organic dye, TDP, into the  $\text{SiO}_2$  network of a gel containing minute crystallites of  $\text{LiNbO}_3$  or  $\text{BaTiO}_3$ .

## 1. Introduction

This grant was awarded in December 1, 1993. The main objective was to prepare two families of advanced ceramic materials based on the liquid solution approach. The first family of advanced ceramics to be synthesized was ferroelectric thin films such as  $\text{BaTiO}_3$  and  $\text{LiNbO}_3$ . The technique selected was the sol-gel method. Under this general heading of "ferroelectrics" it was proposed that three separate but related tasks would be performed. These were (a) the preparation of single crystals, (b) the preparation of amorphous ferroelectrics and (c) the preparation of multilayered structures based on alternating conductive and insulating films. The second family of advanced ceramics to be investigated was supposed to be that based on silicon nitride. However, early in 1994, because of the potential usefulness of Ormosils (organically modified silicates) as thermal insulation for rocket motors and the interests of the Phillips Laboratory at the Edwards Air Force Base, permission was obtained from Captain Hugh de Long to postpone research on silicon nitride and to perform research on the Ormosils instead. This progress report covers the entire period of the grant from 1 December 1993 to 30 November 1998.

## 2. Research on Ormosils

Most of our research on Ormosils are based on the reactions between tetraethoxy silane (TEOS) and polydimethylsiloxane (PDMS). Different ratios of TEOS to PDMS are reacted according to the method shown in Figure 1. In the past four years, our research on Ormosils can be conveniently divided five parts.

### (a) *Structure and Mechanical Properties*

When PDMS is added to TEOS, the mechanical properties of the resultant Ormosils change continuously as shown by Figure 2. Some actual values of mechanical properties are shown in Table 1 for the rubbery Ormosils. At low PDMS concentrations, the Ormosils are hard, brittle solids.

Table 2 shows the values of  $H/K_c$  where  $H$  is the Vickers hardness and  $K_c$  is the fracture toughness. This ratio is defined as the index of brittleness. When the PDMS reaches 10 wt.%, the brittleness of the silica gel has decreased by 50%. These 'hard' Ormosils are some 5 to 8 times harder than most organic plastics. Figure 3 gives the Vickers Hardness as a function of PDMS content. A theory was developed to enable the calculation of hardness. The agreement between experimental and calculated values of hardness is excellent as shown in Figure 3. The structural changes to the silica network as a result of the chemical reaction between TEOS and PDMS are depicted by Figures 4 and 5. The hard Ormosil structure is presented in Figure 4(b) and the rubbery Ormosil structure is given in Figure 5. The rubbery behavior is explained by the mechanism of coiling and uncoiling of the PDMS chains linking the clusters of  $\text{SiO}_2$  as illustrated in Figure 6. At present, various industrial laboratories are evaluating the potentials of hard Ormosils as abrasion resistant coatings for organic plastics.

*(b) High-Temperature stability of Rubbery Ormosils*

Since a rubbery Ormosil may contain as much as 70 wt.% of  $\text{SiO}_2$ , it is natural to inquire as to the possibility of preparing new high temperature stable rubbers with Ormosils. As prepared, the PDMS- $\text{SiO}_2$  rubbery Ormosils would maintain their rubbery property even after a few hours of heating at  $200^\circ\text{C}$  in air. Although this is better than common rubber, it is necessary to inquire why the rubbery behavior of Ormosils should be lost at temperatures in excess of  $200^\circ\text{C}$  and if there are methods to make improvements of the high temperature stability. During the period of this grant, we discovered that very small amounts of iron added to the original Ormosil liquid solution in the form of  $\text{FeCl}_3$  or  $\text{Fe}_2\text{O}_3$ , can increase the thermal stability of Ormosil very significantly. Figure 7 shows the remarkable effects of small amounts of Fe. The presence of Fe appears to be ineffective in  $\text{N}_2$ . It may therefore be presumed that the oxidation of the  $\text{CH}_3$  groups on the PDMS chains causes the loss of rubbery elasticity. Iron is also known to endow high temperature

Table 1 - Mechanical Properties of Rubbery Ormosils at 20°C

Samples	Density (g/cm <sup>3</sup> )	Tensile Strength (MPa)	Elongation (%)	Elastic Modulus (MPa)	Resilience (%)
TEOS/PDMS <sub>1700</sub>	0.46	2.15	24.5	19.2	47
Aerosil ox50-TEOS/PDMS <sub>1700</sub> **	0.79	0.86	42.6	3.0	69
Aerosil 90*-TEOS/PDMS <sub>1700</sub>	0.83	1.58	38.3	7.0	72
Aerosil 150-TEOS/PDMS <sub>1700</sub>	0.87	1.58	33.2	7.8	73
Aerosil 200-TEOS/PDMS <sub>1700</sub>	0.91	1.63	23.2	11.7	72
Aerosil ox50-TEOS/PDMS <sub>4200</sub>	0.79	1.15	51.3	4.0	69
Aerosil 90-TEOS/PDMS <sub>4200</sub>	0.80	1.82	49.6	10.0	70
Aerosil 150-TEOS/PDMS <sub>4200</sub>	0.81	2.25	34.7	11.5	72
Aerosil 200-TEOS/PDMS <sub>4200</sub>	0.84	2.41	34.7	13.5	72

\* The number for each Aerosil type indicates the BET surface area  $\pm 15$  in units of m<sup>2</sup>/g.

The average primary particle sizes of Aerosils in nm are 40, 20, 14 and 12 for Aerosil ox50, 90, 150 and 200, respectively.

\*\* The subscripts 1700 and 4200 are the molecular weights of PDMS<sub>1700</sub> and PDMS<sub>4200</sub>, respectively.

Table 2 Indices of Brittleness of the Hard Ormosils

Wt.% of PDMS	0	3	5	8	10
Mol.% of [Si(CH <sub>3</sub> ) <sub>2</sub> O]	0	7.9	12.8	19.5	23.7
Fracture toughness (Mpa m <sup>1/2</sup> )	0.501 ± 0.002	0.492 ± 0.002	0.479 ± 0.001	0.465 ± 0.001	0.460 ± 0.001
Brittleness (μm <sup>-1/2</sup> )	3.63 ± 0.15	3.19 ± 0.13	2.86 ± 0.11	2.32 ± 0.12	1.88 ± 0.12



stability in organic polymers. It has been suggested that some of the iron ions exist in the  $\text{Fe}^{2+}$  state. These  $\text{Fe}^{2+}$  ions will use up oxygen molecules and convert to  $\text{Fe}^{3+}$  state and thus less oxygen will be available to react with the  $\text{CH}_3$  groups. This type of explanation is unsatisfactory since the ratio of the amount of Fe ions to  $\text{CH}_3$  groups can be only 0.001 and the Fe is already effective (see Figure 7). At present, an acceptable mechanism for the effective influence of Fe ions is not known. We have found that another transition metal ion, vanadium, is also effective in enhancing high temperature stability although it is not as pronounced as Fe.

(c) *Ormosils as High Temperature Insulators - Collaboration with Edwards Air Force Base*

During this grant period, we have collaborated with Dr. J. Lichtenhan of the Phillips Laboratory at the Edwards Air Force Base to fabricate and to test Ormosils as insulators for rocket motors. Large sheets of Ormosils were fabricated and submitted to the Phillips Laboratory for testing. Such samples are shown in Figure 8. The testing method is illustrated in Figure 9. The initial results were promising. However, the tensile strengths of the Ormosil samples were relatively low and created a problem for handling when the insulation is applied to the rocket motor casing. Because of the lack of human resources we were unable to continue with experiments to strengthen the Ormosils which remain to be a promising family of insulation materials for high temperature applications.

(d) *Additions of Carbon Black to Ormosils*

Because the additions of carbon black to organic rubber can cause large changes of mechanical properties, it was logical to consider the effects on Ormosils. Three types of carbon black were obtained from the Degussa Corporation: SB4, SB5 and FW200 have average particle sizes of 25, 20 and 13 nm, respectively. It was impossible to add more than 3 wt.% of carbon black

to the Ormosil solution because of agglomeration. The method developed is shown in Figure 10. The compositions studied and the density and porosity results of the filled Ormosils are shown in Table 3. Samples containing the FE200 were blue in color, presumably because of Rayleigh Scattering from the ultrafine carbon particles (13 nm). The samples containing the larger carbon particles were gray in color resulting from a combination of scattering and absorption. The mechanical properties of Ormosils were found to be significantly influenced by the concentration and the size of the carbon black particles. Table 4 shows the FW200 can affect the tensile strength, elongation and elastic modulus of Ormosils more than the larger particle carbons. Table 5 shows the influence of carbon concentration. In Figure 11, tensile strength is plotted against carbon black concentration and in Figure 12, resilience is shown as a function of carbon black type and concentration.

Although both the tensile strengths and resilience of Ormosils can be increased significantly via the addition of 2 wt.% of carbon black, the increases are relatively minor as compared to the influence of carbon black on common organic rubbers. Secondly, the process shown by Figure 10 is highly complex and it will not be cost-effective for large scale preparation. Much more research will have to be done if serious applications of Ormosils are contemplated in the future.

#### (e) *Rubbery Aerogels*

Aerogels made from the supercritical drying of  $\text{SiO}_2$  gels can have more than 99% porosity and are known as the best thermal insulator ever synthesized. Because of the brittleness of  $\text{SiO}_2$  and the low mechanical strengths of such a porous solid, aerogels have not been used widely as a thermal insulator. Since the brittleness of silica gel can be greatly reduced by network structural modification via the incorporation of polydimethylsiloxane PDMS chains, this research was undertaken to study the preparation and properties of rubbery "aero-Ormosils" or "Aeromosil." Two methods were developed to synthesize these new materials and shown

**Table 3      Density and Porosity of Carbon Black filled ORMOSILs**

Material	Measured Density $\rho_b$ (gm/cm <sup>3</sup> )	Calculated Fully Dense Material Density $\rho_1$ (g/cm <sup>3</sup> )	Calculated Porosity $\rho_1$ (g/cm <sup>3</sup> )
60/40 ORMOSIL	0.45	1.29	0.65
ORMOSIL with 1 wt.% SB4	0.49	1.30	0.62
ORMOSIL with 2 wt.% SB4	0.56	1.31	0.57
ORMOSIL with 3 wt.% SB4	0.58	1.32	0.56
ORMOSIL with 2 wt.% SB5	0.89	1.31	0.48
ORMOSIL with 1 wt.% FW200	0.75	1.30	0.42
ORMOSIL with 2wt.% FW200	1.01	1.31	0.23
ORMOSIL with 3 wt.% FW200	1.03	1.32	0.22

**Table 4      Mechanical Properties of FW200, SB5, and SB4 ORMOSILs**

Material	Strength (Mpa)	Elongation (%)	Elastic Modulus (MPa)
ORMOSIL with 2 wt.% FW200 (primary particle size: 13nm)	2.50	4.50	27.4
ORMOSIL with 2 wt.% SB5 (primary particle size: 20 nm)	1.05	5.8	10.3
ORMOSIL with 2 wt.% SB4 (primary particle size: 25 nm)	0.89	16.1	8.1

**Table 5      Mechanical Properties of ORMOSILs with Increasing Loading**

Material	Strength (MPa)	Elongation (%)	Elastic Modulus (MPa)
ORMOSIL with 1 wt.% SB4	0.64	8.1	5.8
ORMOSIL with 2 wt.% SB4	0.89	15.1	8.1
ORMOSIL with 3 wt.% SB4	0.90	16.1	8.1
ORMOSIL with 1 wt.% FW200	1.40	11.2	23.6
ORMOSIL with 2 wt.% FW200	2.50	4.5	27.4
ORMOSIL with 3 wt.% FW200	2.58	4.5	29.9

in Figure 13. The supercritical drying equipment is shown in Figure 14. The bulk density, porosity and specific surface area of some aeromosils are shown in Table 6. Pore size distributions for the acid and the acid/base catalyzed samples are shown in Figure 15. That the Aeromosils are indeed rubbery is shown in the three photographs of Figure 16. The sample is shown to have been reduced in length by 25% and then recovered fully. A tentative model to explain this rubbery behavior is presented in Figure 17. Rubbery Aerogels are thus a reality. For practical applications, a method will have to be developed for the cost-effective production of rubbery aerogel pellets rather than sheets.

### 3. Research on Ferroelectrics

Our research on ferroelectrics via the sol-gel method has been concentrated on both crystalline and amorphous thin films. The program is basically a continuation of our previous effort under AFOSR-91-0096 which terminated on 30 November 1993. The most important aspect of our program is the discovery of ferroelectricity in new organic-inorganic hybrid materials. Our program is summarized in the four separate sections below.

#### (a) *Single Crystal Ferroelectrics*

Single crystalline films of  $\text{KNbO}_3$  were successfully grown epitaxially on  $\text{MgO}$  and  $\text{SrTiO}_3$  substrates. Figure 18 shows the lattice fringe image of  $\text{KNbO}_3$  on  $\text{SrTiO}_3$ . Narrow channels were etched into the films to form waveguides as shown in Figure 19. Infrared laser beams of  $1.06 \mu\text{m}$  were directed into the film and green light of  $0.532 \mu\text{m}$  was generated via second harmonic modes. Fe was also introduced into the sol-gel solutions as dopants for the  $\text{KNbO}_3$ . The third-order susceptibility of the doped film now enabled the intensity amplification of laser light as shown in Figure 20. We have therefore demonstrated conclusively that the sol-gel method can be used to fabricate ferroelectric single crystal films with useful second-order and third-order nonlinear optical properties.

Table 6 Bulk density with corresponding porosity and specific surface area with linear correlation coefficient from BET

Sample	Density (g/cm <sup>3</sup> )	Porosity (% theory)	SSA (m <sup>2</sup> /g)	Correlation
OA2	0.071	96.8	1169	0.9969
10A3	0.061	97.2	1370	0.9993
10A2	0.059	96.6	1274	0.9990
10A3	0.057	96.7	1193	0.9990
20A2	0.066	95.6	818	0.9997
20A3	0.051	96.6	786	0.9993
0AB2	0.079	96.4	1103	0.9991
10AB2	0.099	94.3	920	0.9995
20AB2	0.150	90.1	659	0.9996

### *(b) Multilayered Thin Film Structures*

It has been proven for covalent semiconductors that a multilayered structure consisting of alternating layers of insulator and semiconductor can result in a "quantum well." Such quantum wells hold promise for many devices in photonics. The equivalent multilayered structures with oxides had not been fabricated. During this grant period, an automatic dip-coating equipment was designed and constructed (Figure 21). Two solutions A and B are placed in separate containers standing on a rotating platform. The substrate first dips into A and is then hoisted slowly upwards into a furnace. After the film A is heat-treated, the substrate is then lowered into solution B and the process repeated. The speed of the dipping can be controlled. We were able to prepare multilayers of amorphous  $\text{BaTiO}_3$  and  $\text{SiO}_2$  to test the utility of the equipment. Up to 12 pairs of films with thickness of the order or  $300\text{\AA}$  each were fabricated as shown in Figure 22. The optical quality of the stack was excellent. Due to the shortage of human resources, we were unable to continue with this program.

### *(c) Amorphous Ferroelectric Films*

In our previous AFOSR Grant No. AFOSR-91-0096 we first reported that amorphous  $\text{LiNbO}_3$  film prepared by the sol-gel method exhibited ferroelectric behavior. During this period such "amorphous ferroelectricity" was confirmed for  $\text{BaTiO}_3$  and PZT. The presence of "ferrons"--extremely small crystals of the order of  $20\text{\AA}$ --was confirmed by high resolution electron microscopy and proposed to be responsible for the observed ferroelectric behavior. A model was generated to account for this anomalous behavior. The model involves the coupling of dipoles via ferrons and the non-crystalline part of the solid network as illustrated in Figure 23. A comparison of experimental ferroelectric properties and those calculated based on this model was very satisfactory as presented in Table 7. Table 8 gives a comparison of the properties of polycrystalline film, amorphous film and

Table 7- Theoretical results in comparison with  
experimental results

	PZT		BaTiO <sub>3</sub>	
	<i>Theoretical</i>	<i>Experimental</i>	<i>Theoretical</i>	<i>Experimental</i>
Free energy G-G <sub>0</sub> (J/mol)	-38	no	-3.7	no
Averaged value of dipole moments of ferrons, $\langle \mu_z \rangle$ , (10 <sup>-28</sup> C cm)	17.2	22.55 (crystal)	7.8	17.7 (crystal)
Remanent polarization $P_r$ ( $\mu\text{C}/\text{cm}^2$ ) from statistical thermodynamics	3.2	3.2	2.3	2.3
Remanent polarization $P_r$ ( $\mu\text{C}/\text{cm}^2$ ) from statistical physics	3.9	3.2	2.1	2.3
Coercive field $E_c$ (10 <sup>4</sup> V/cm)	5.0	7.8	6.5	10.5
Permittivity of ferrons $\epsilon_r$	no	1850 (crystal)	no	210 (crystal)
Permittivity of porous matrix $\epsilon_r$	98	160 (overall)	75	90 (overall)
Permittivity of dense matrix $\epsilon_r$	165	no	140	no
Volume fraction of ferron $v_1$ (%)	16.3	10 or more (HRTEM)	17.6	10 or more (HRTEM)
Porosity of overall film $v_p$ (%)	9.2	no	10.3	no
Refractive index of ferrons $\eta_F$	no	2.70 (crystal)	no	2.40 (crystal)
Refractive index of dense matrix $\eta_s$	2.32	no	2.23	no
Refractive index of porous matrix $\eta_m$	2.1	2.1	2.0	2.0

**Table 8** Electrical Properties of Polycrystalline and Amorphous BaTiO<sub>3</sub> Thin Films at Room Temperature (Some data of Ceramic bulk are listed for comparison)

Properties	Polycrystalline (850°C/6h)	Amorphous (400°C/1h)	Ceramic Bulk (1450°C/1h)*
Film's thickness $t$	0.3 mm	0.3 mm	
Average grain size (Å)	1000	no grains were	> 4000
Dielectric permittivity $\epsilon$ (25°C)	210 (1 kHz)	90 (1 kHz)	1400 (1kHz)
Resistivity (d.c.) $\rho$ ( $\Omega\text{cm}$ )	$5.5 \times 10^9$	$1.5 \times 10^9$	**
Pyroelectric coefficient $\rho$ (nC/cm <sup>2</sup> K)	10	0.5	20
Remanent polarization $P_r$ (C/cm <sup>2</sup> )	19	2.3	26
Coercive field $E_c$ (kV/mm)	10	10	
Breakdown strength $E_b$ (kV/mm)	800	> 60	**
Optical refractive index $n$	2.3	2.0	2.43 ( $n_o$ )*** 2.37 ( $n_e$ )***

\* Data come from Ref. [1]

\*\* Depends on dopants and processing

\*\*\* Data from single crystal



bulk ceramic  $\text{BaTiO}_3$ . The amorphous ferroelectric film appears to be a "weak" or "soft" ferroelectric.

(d) *Organic-Inorganic Hybrids*

During this grant period, we prepared thin amorphous films from solutions containing the double alkoxides of  $\text{LiNbO}_3$  (and/or  $\text{BaTiO}_3$ ) as well as TEOS. Our gelation and drying, the films manifested ferroelectric behavior and "ferrons" were again observed. This prompted us to examine gels made from solutions containing the  $\text{LiNbO}_3$  (and/or  $\text{BaTiO}_3$ ) double alkoxide, TEOS and TDP, a complex dye the structure of which is shown in Figure 24. On gelation, the TDP and TEOS would yield a silica network and ferrons of the  $\text{LiNbO}_3$  (and/or  $\text{BaTiO}_3$ ) would be trapped in the network. Electrical interactions would perhaps be possible between the ferrons as depicted in Figure 25. Ferroelectric behavior was indeed observed as shown by the P-E hysteresis loop in Figure 26. Ferrons were also revealed by high resolution electron microscopy as shown in Figure 27. We also discovered that the interactions between TDP and  $\text{LiNbO}_3$  and  $\text{BaTiO}_3$  are different as shown by the color difference of the films in Figure 28. The reasons for the different behavior of  $\text{LiNbO}_3$  and  $\text{BaTiO}_3$  are not known and investigations are ongoing. These organic-inorganic hybrids constitute a new family of electronic materials and are worthy of further studies.

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## 5. Student Training

During this grant period, the following graduate students have received their M.S. and Ph.D. degrees through the support of this grant.

### (a) *M.S. Degree Recipients*

Justine Y. Tseng  
Eva M. Wong  
Giovanni Minervi  
Yudan Lou  
Stephen J. Kramer  
Soon-Ku Yuh  
John Gonzalez  
Amy Roschelle  
Tammy Chau  
Yasukazu Hoshino  
Brady Shih  
Charles Q. Wu  
Phillip Wong

(b) *Ph.D. Degree Recipients*

Kevin J. Thorne  
C.-Y. Li  
S.S. Park  
Yuhuan Xu  
Ken C.H. Cheng  
Eric P. Bescher

6. **Postdoctoral Scholars and Visitors**

Dr. Fausto Alonso (Spain)  
Dr. I.C. Ho (Taiwan)  
Dr. H. Unuma (Japan)  
Ms. Yu Ling (PRC)  
Dr. Q. Huang  
Dr. Yuhuan Xu  
Dr. S.S. Park (Korea)  
Dr. A. Matucci (Italy)  
Dr. F. del Monte (Spain)  
Dr. H. Inoue (Japan)

7. **Professional Activities and Recognition**

Professor J.D. Mackenzie was organizer and chair of Sol-Gel Optics III and IV in 1994 and 1997, respectively for SPIE. These international conferences attract an audience of 200-300 people and are now well recognized by scientists and engineers involved in optical materials. Professor Mackenzie continued to be an active member of the International Advisory Committee which organizes the Workshop on Sol-Gel Science and Technology. The last two workshops were in Portugal (1995) and in the United Kingdom (1997). Professor Mackenzie was named Cecil and Ida Green Honors Professor by Texas Christian University in May, 1994, the Samuel S. Scholes Lecturer by Alfred University, Alfred, New York in March, 1995 and the W.E.S. Turner Lecturer by Sheffield University, Sheffield, U.K. in May, 1996.

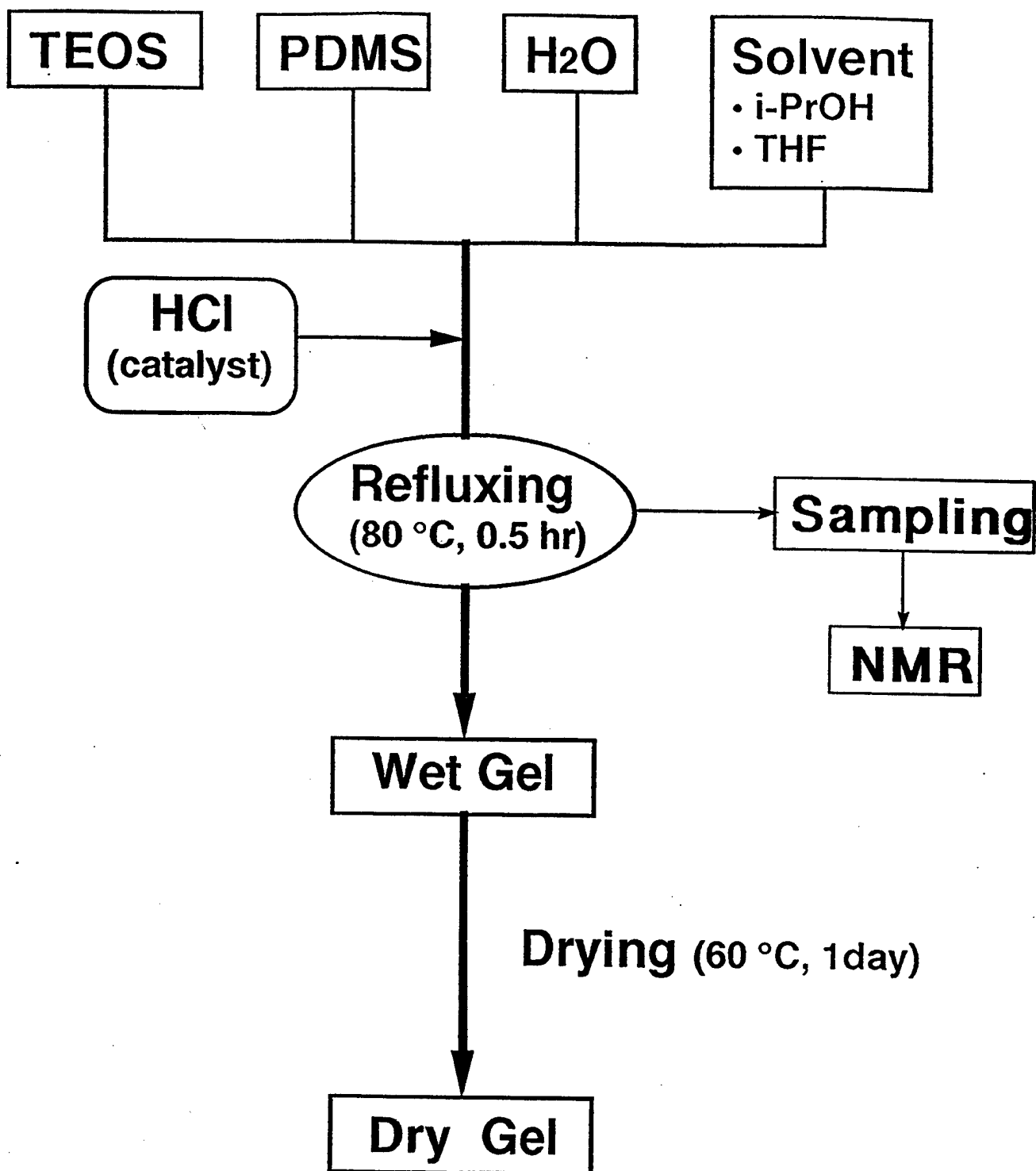
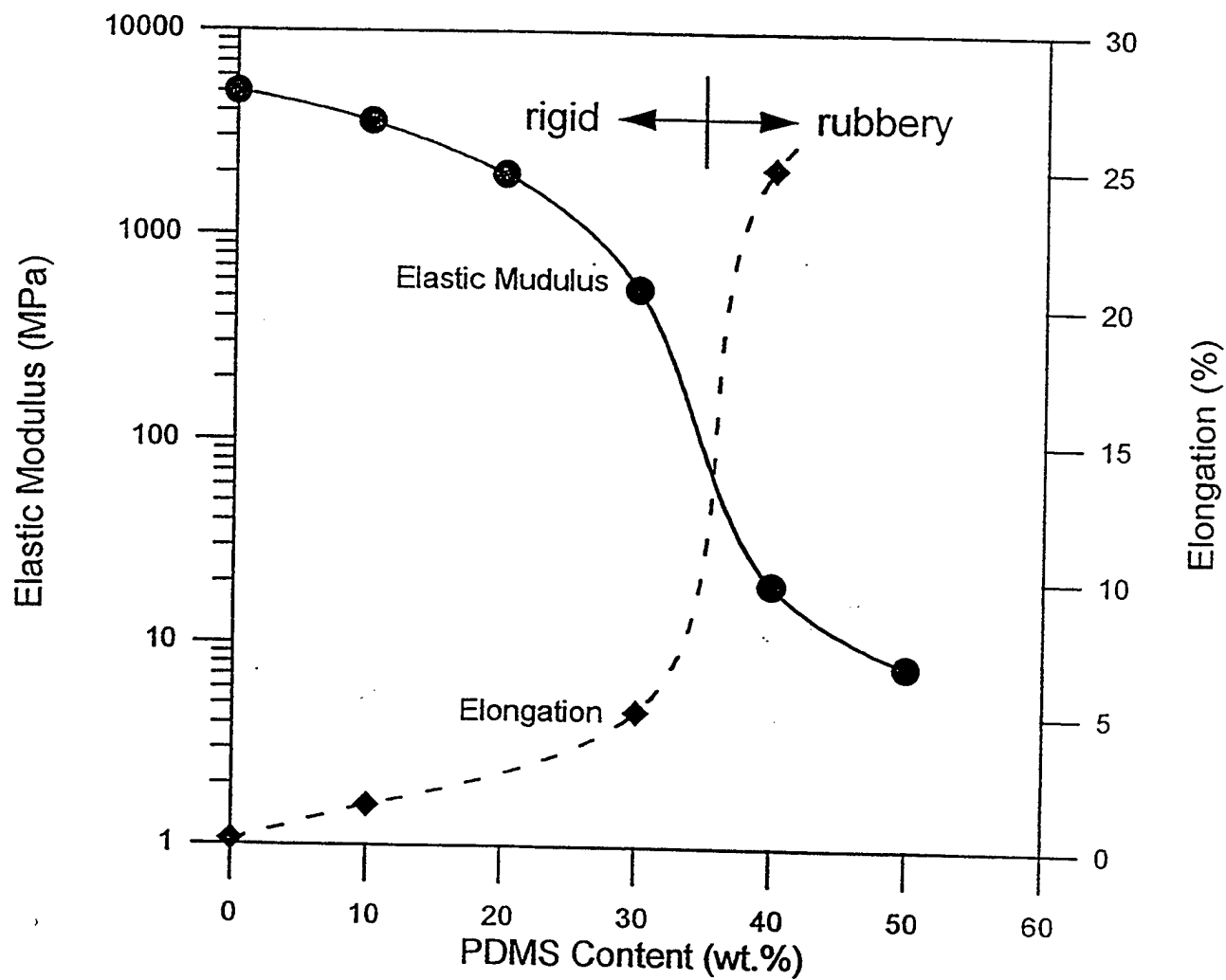


Figure 1 Flow sheet of preparing ORMOSILs through refluxing process





**Figure 2** Variation of mechanical properties of Ormosils as a function of PDMS content

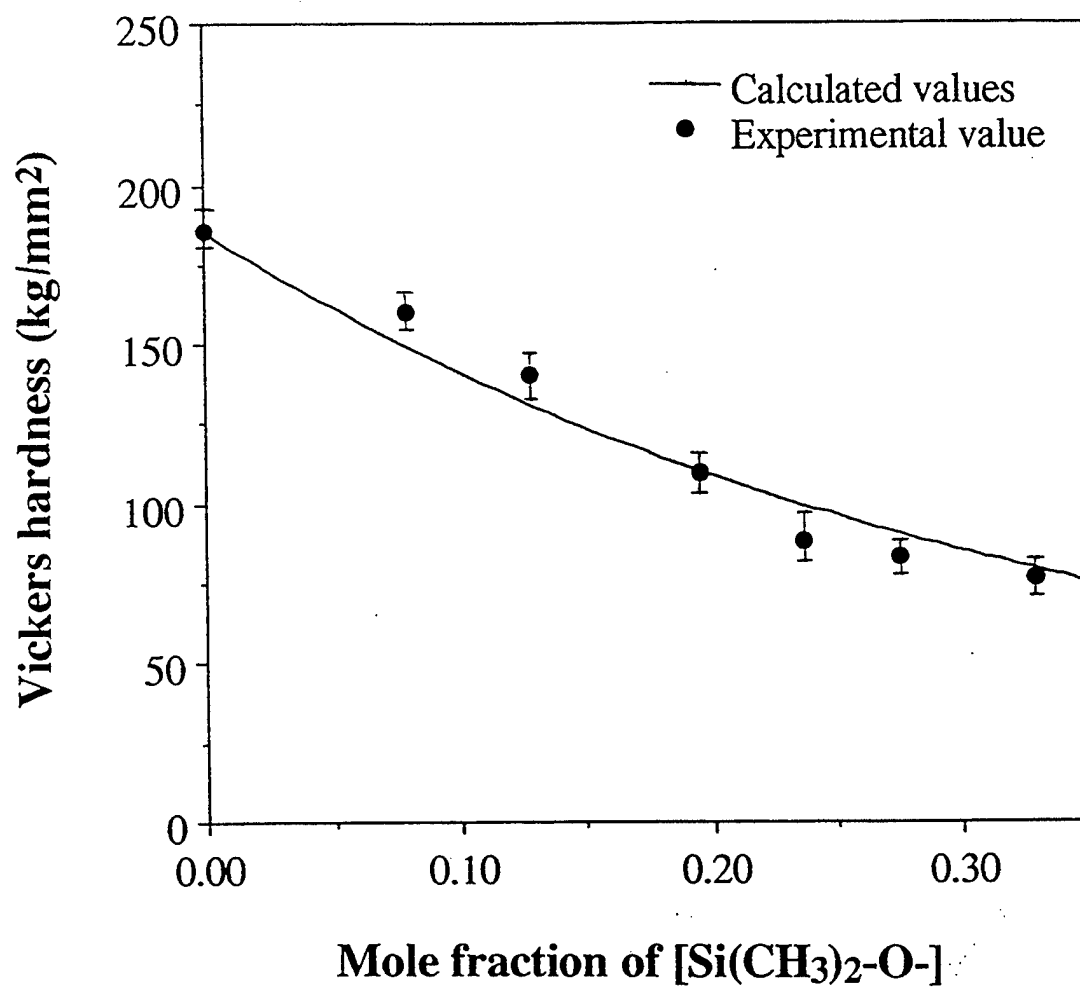


Figure 3

Vickers hardnesses of the TEOS/PDMS system hard ormosils

Figure 4 Modification of the Random Network Structure of SiO<sub>2</sub> by PDMS

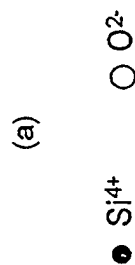
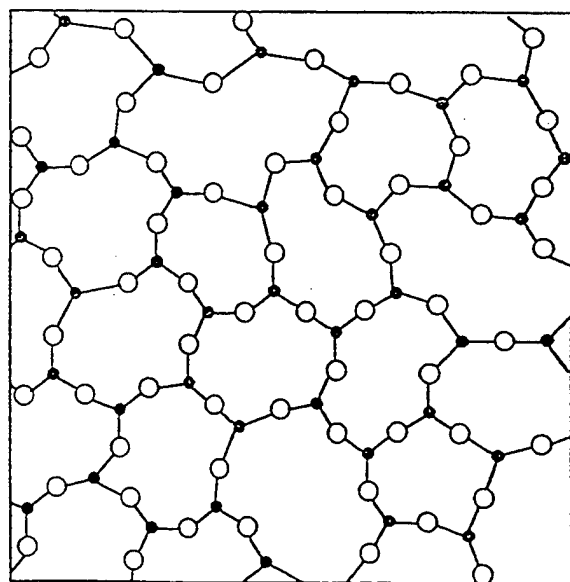
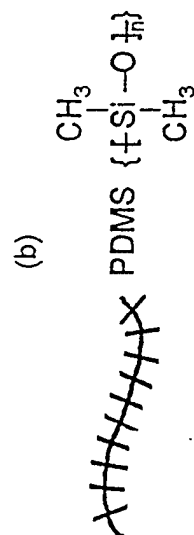
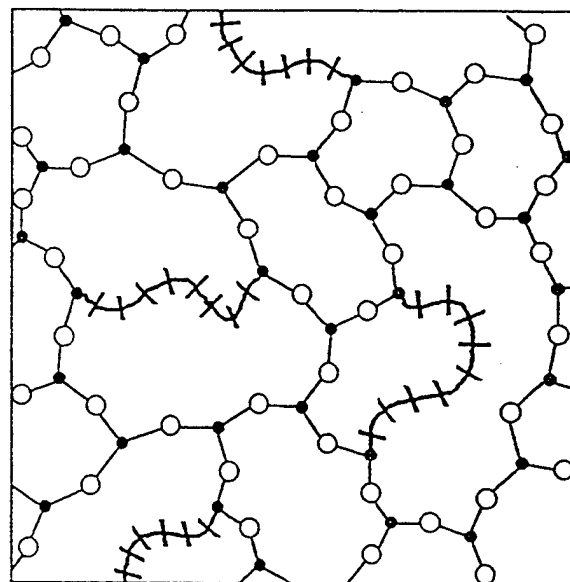
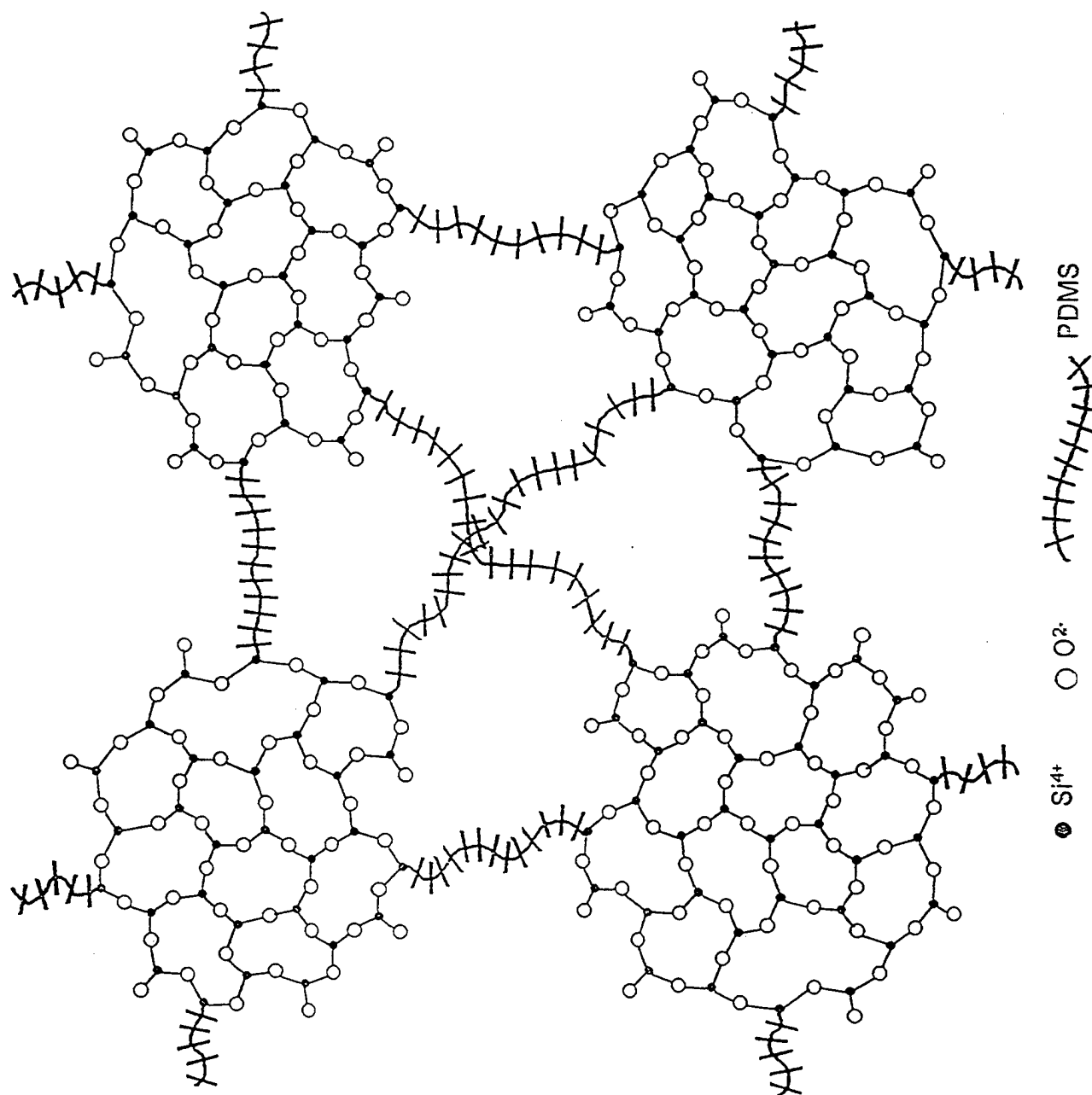
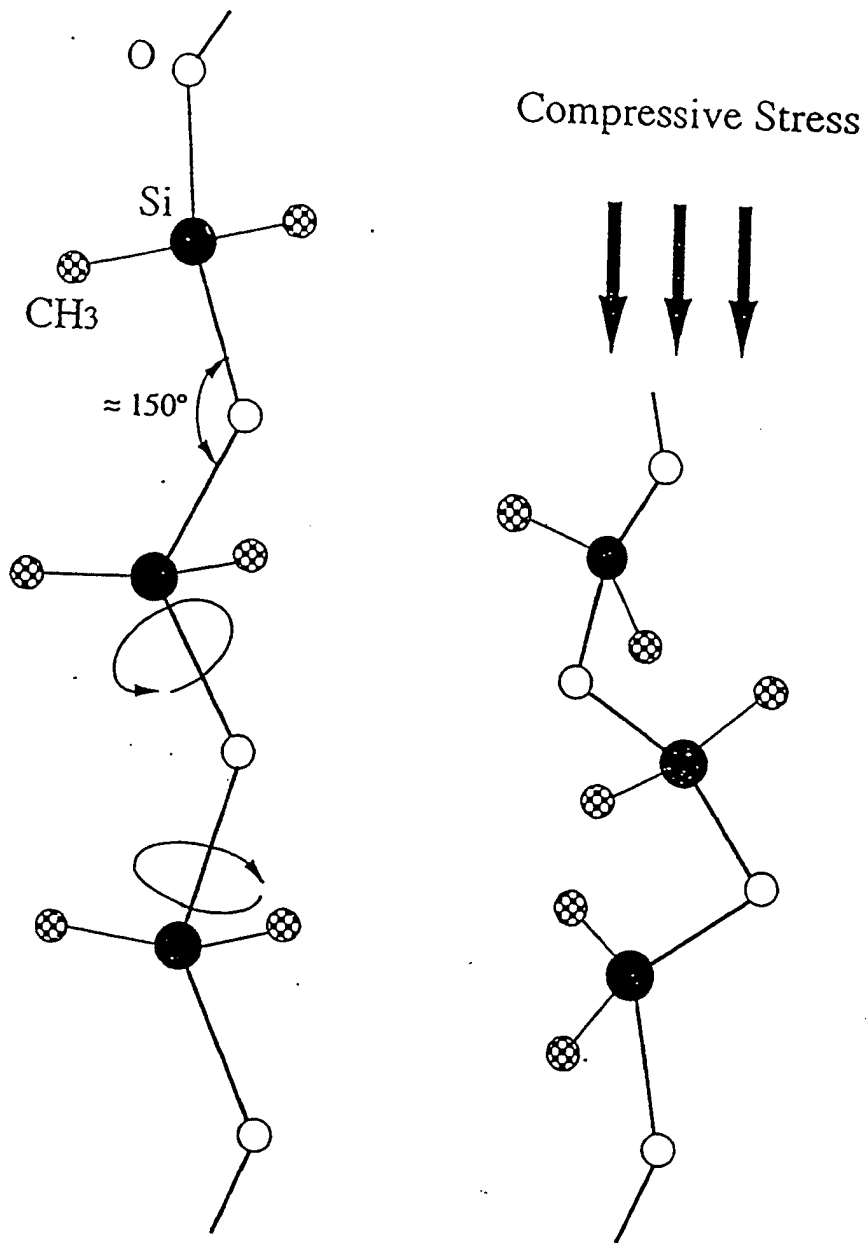


Figure 5 Rubbery Ormosil from High Concentrations of PDMS in  $\text{SiO}_2$





Chain can be shortened by rotation around Si-O-Si

Figure 6 Coiling of PDMS chains

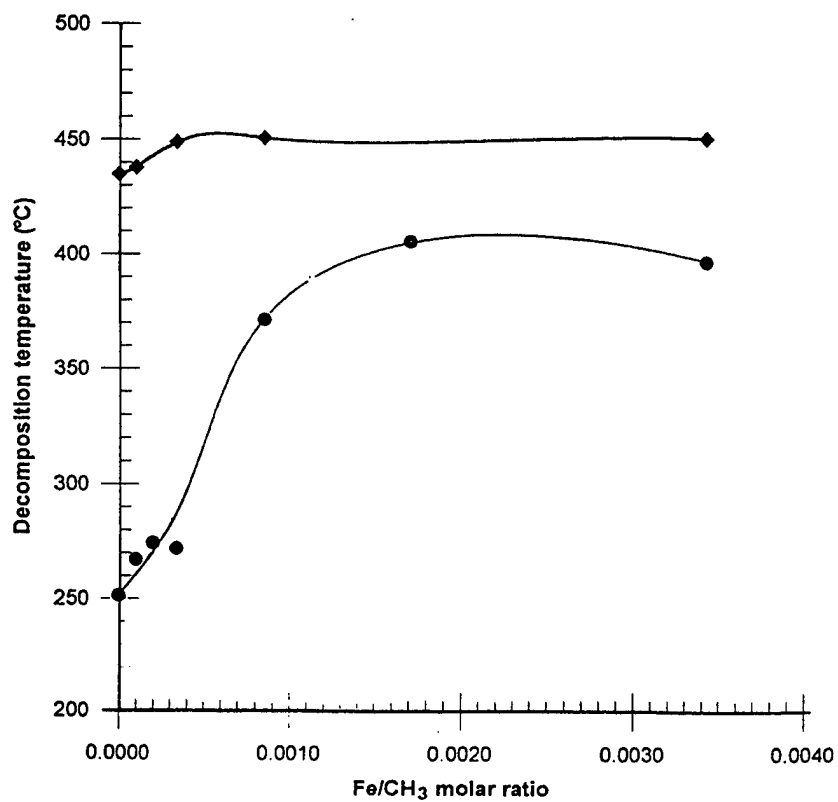


Figure 7 Effect of iron on thermal decomposition temperature, by TGA, of ORMOSILs in air (bottom curve) and in nitrogen

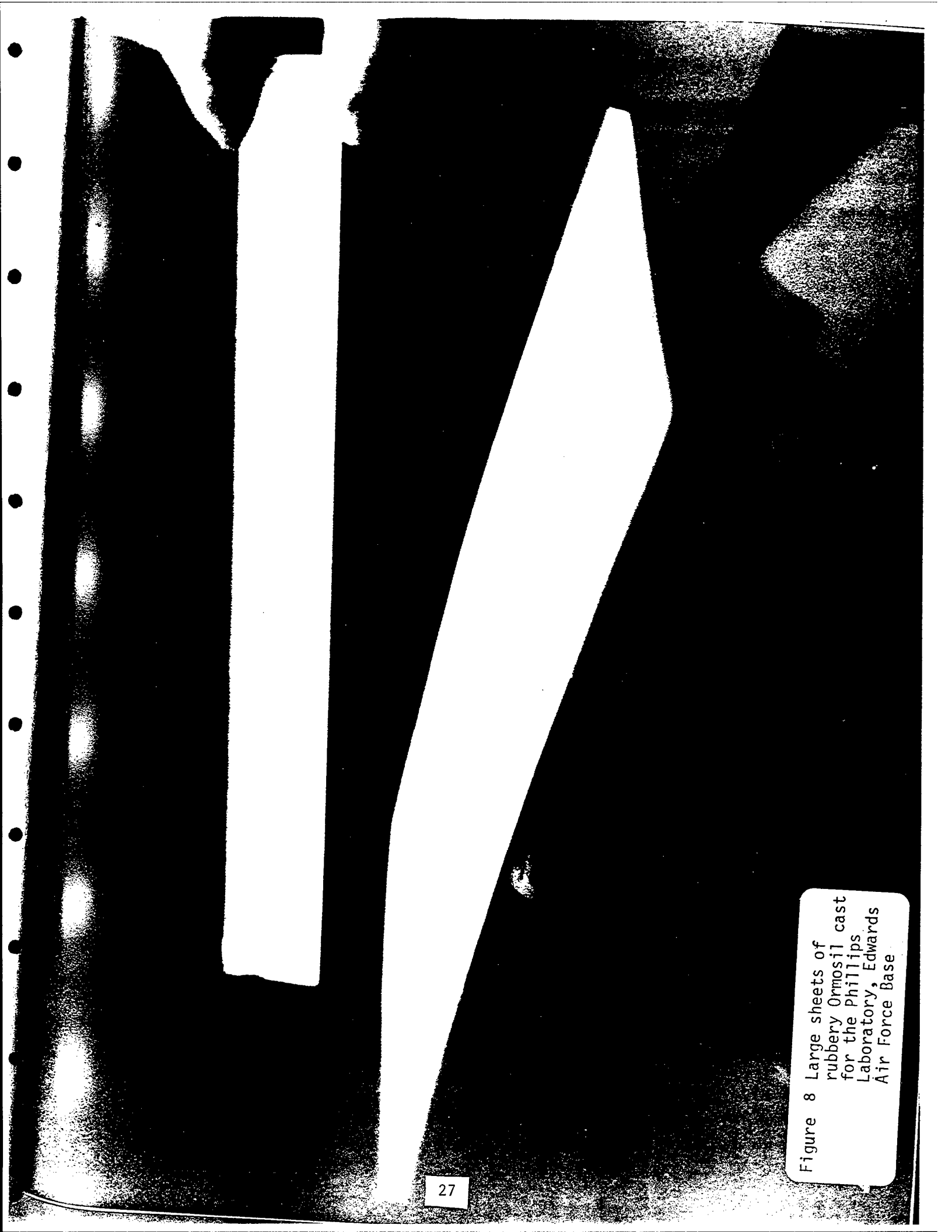
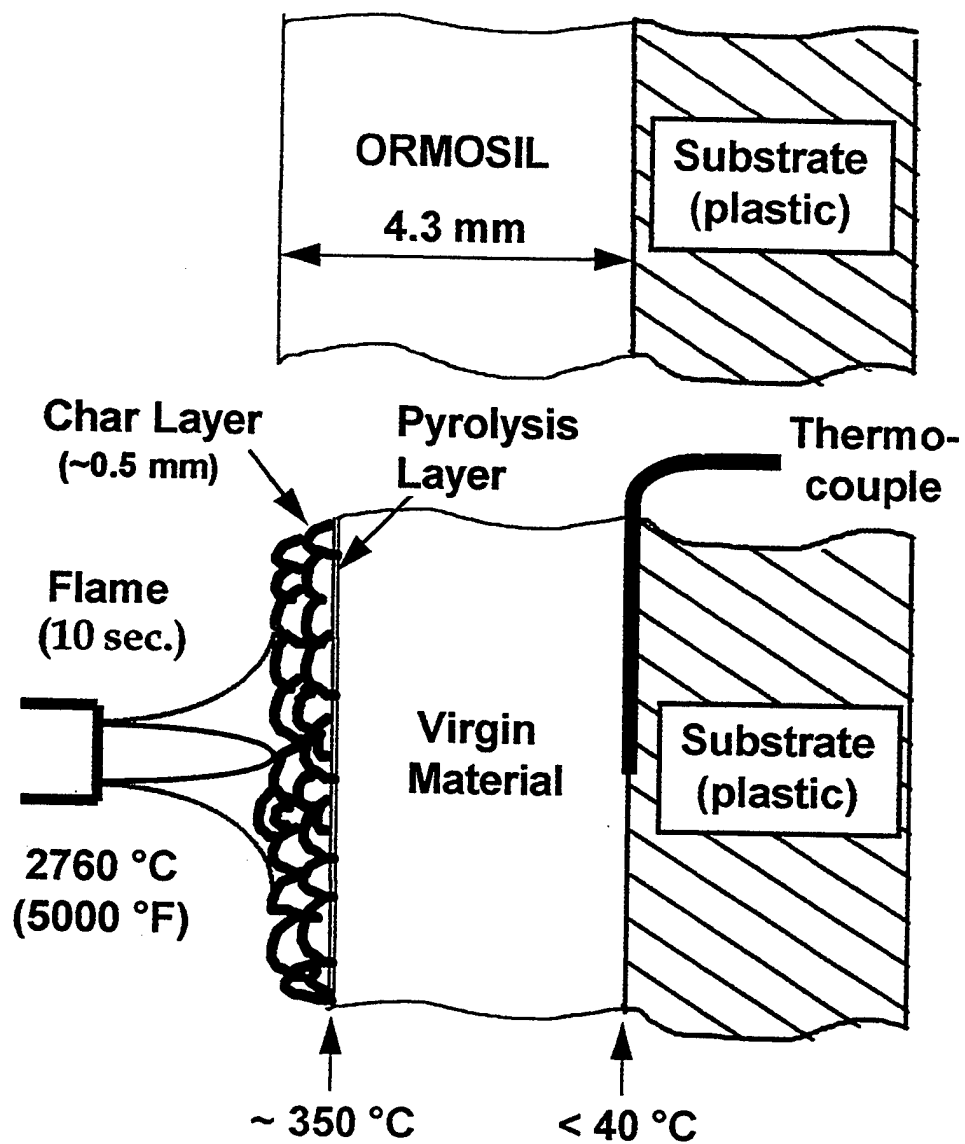


Figure 8 Large sheets of  
rubbery Ormosil cast  
for the Phillips  
Laboratory, Edwards  
Air Force Base



**Figure 9** Insulating mechanism of ORMOSIL against extremely high temperature flame



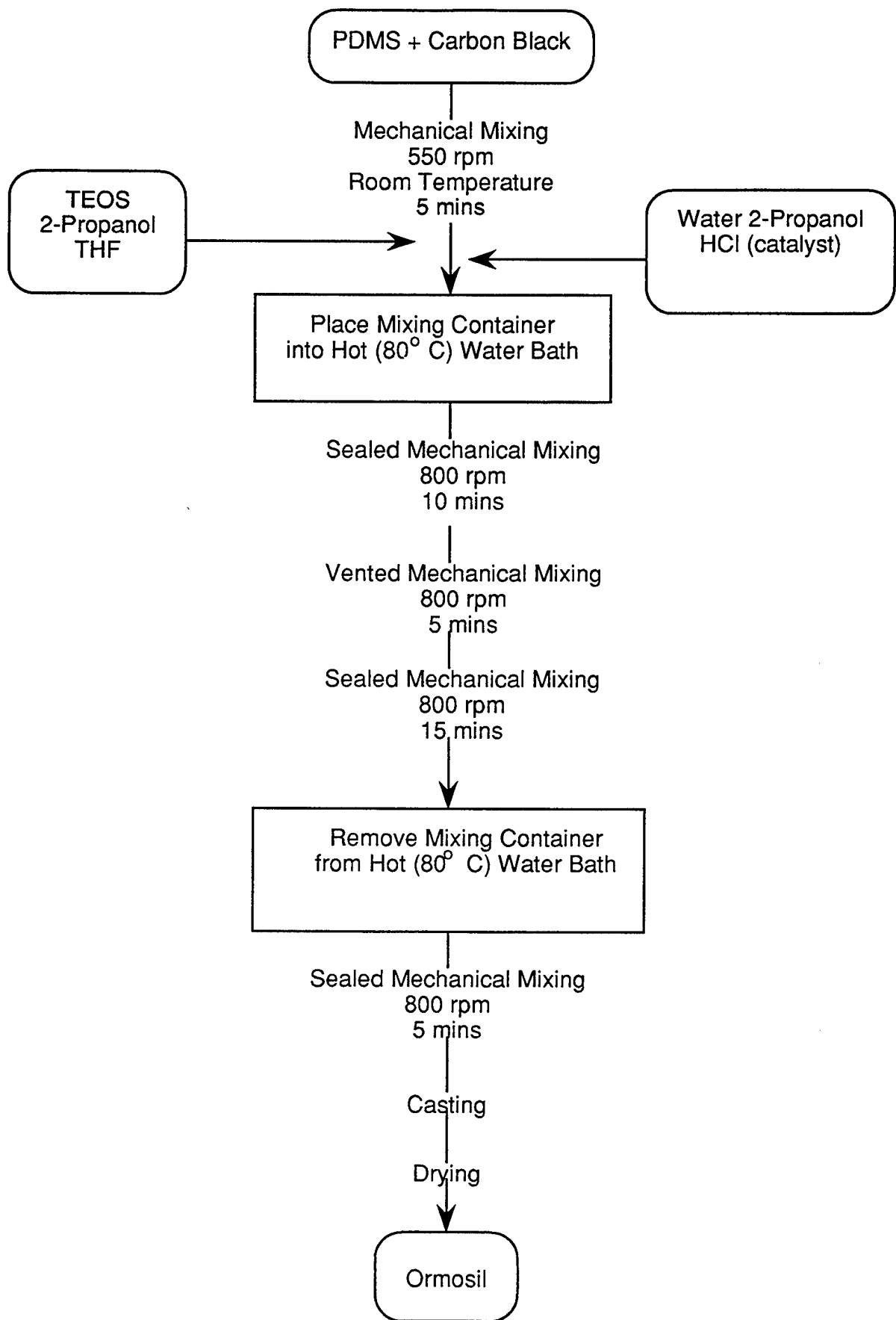
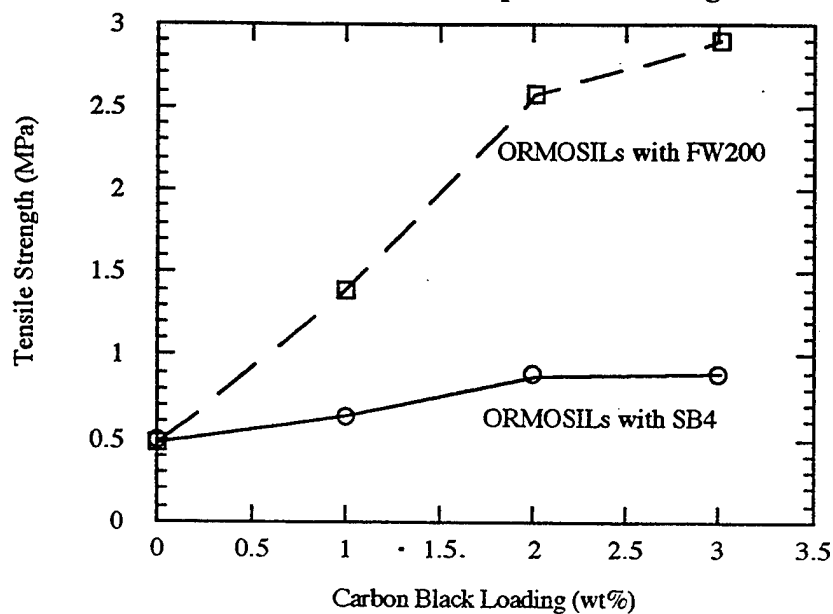


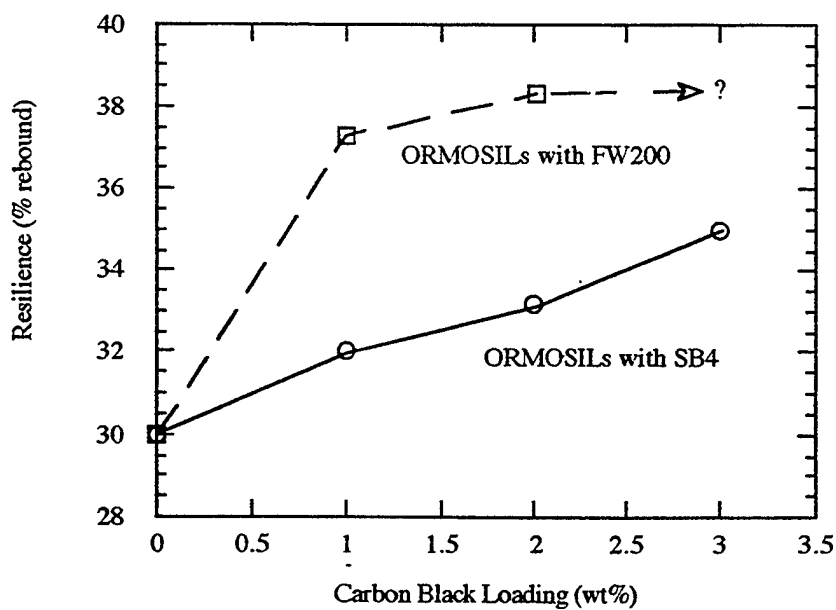
Figure 10 Flow chart for mechanical mixing

**Tensile strengths of carbon black filled ORMOSILs  
as a function of percent loading**



**Figure 11**

**Resilience of carbon black filled ORMOSILs  
as a function of percent loading**



**Figure 12**

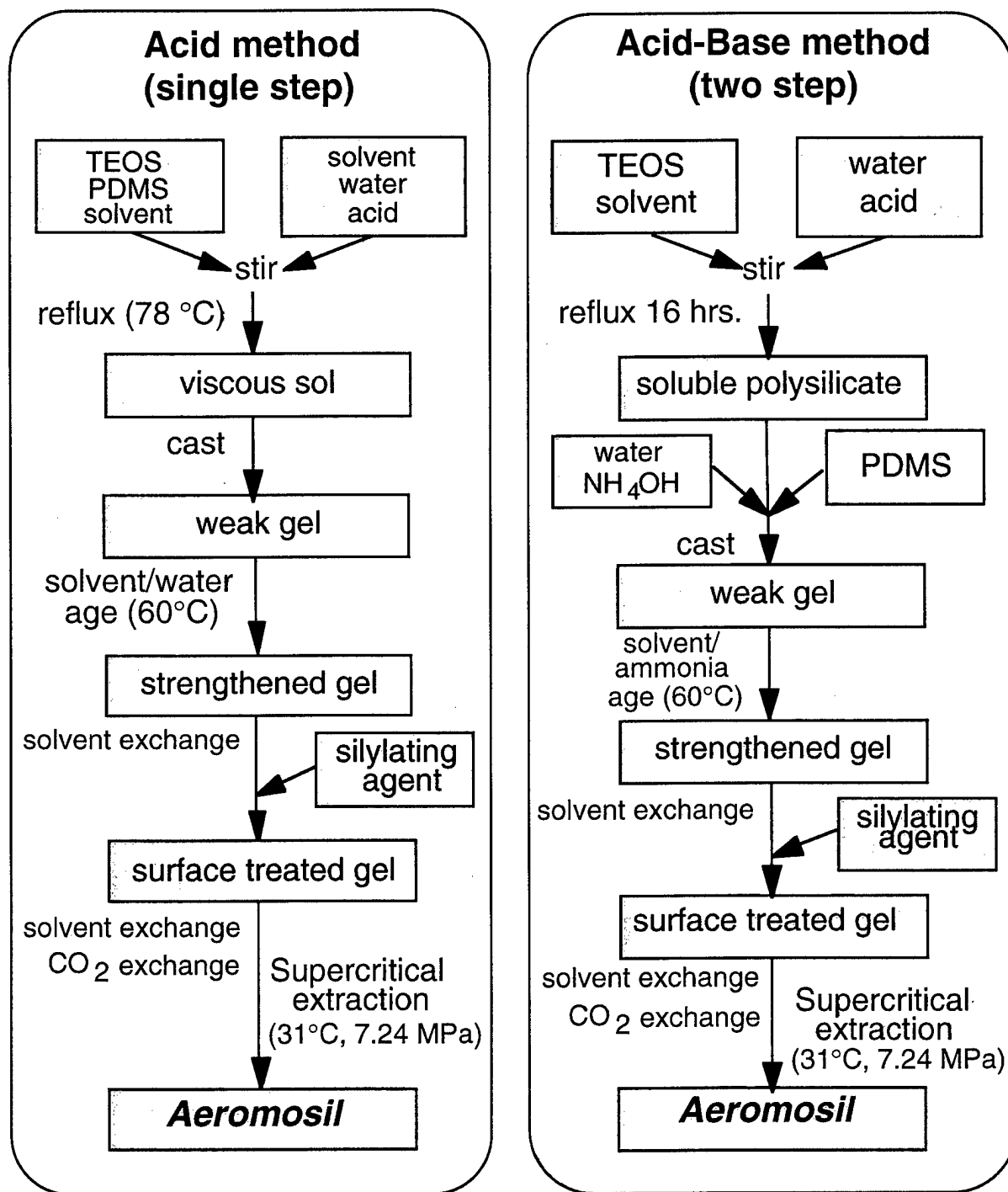


Figure 13 Flow chart schematic of acid and acid-base catalyzed Aeromosil formation

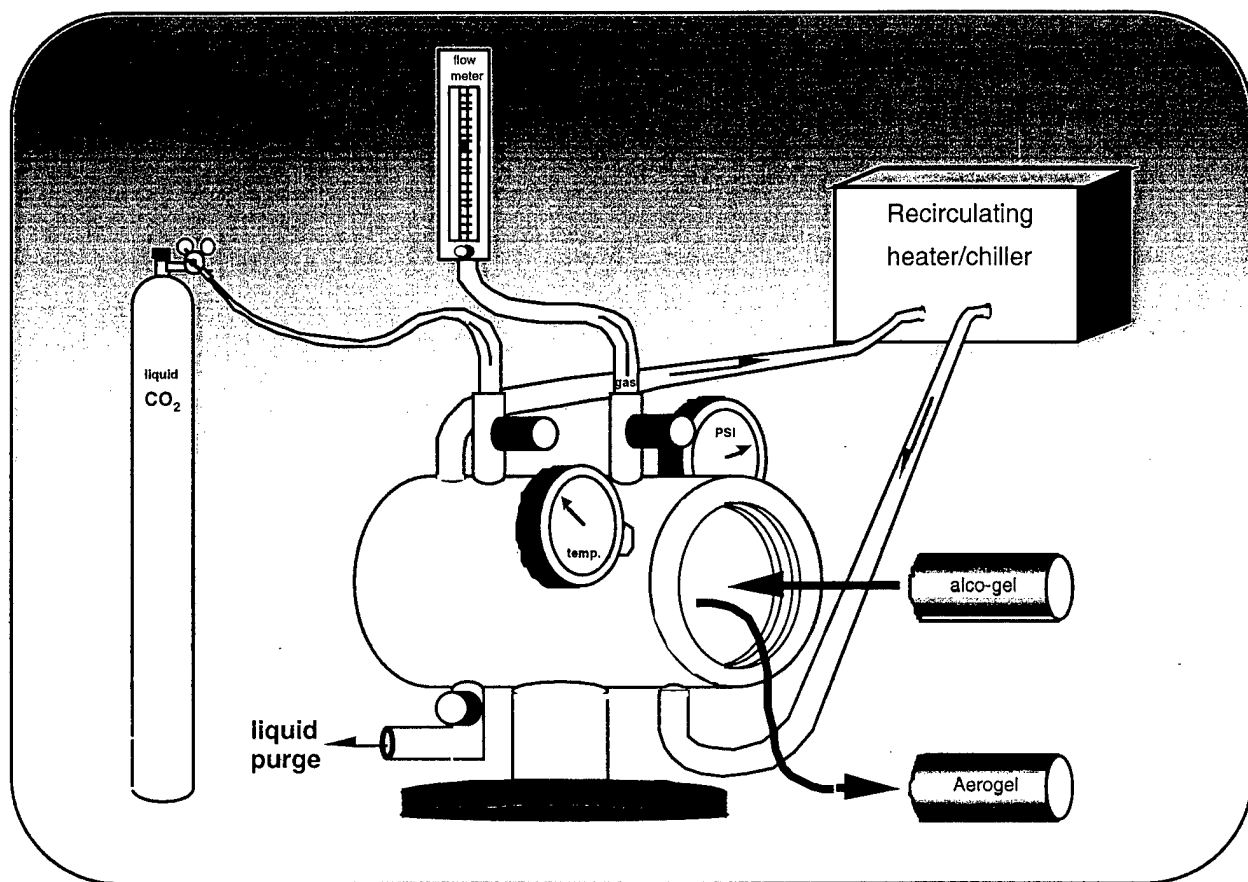


Figure 14 Schematic representation of a supercritical drying apparatus used to make rubbery Aeromosils

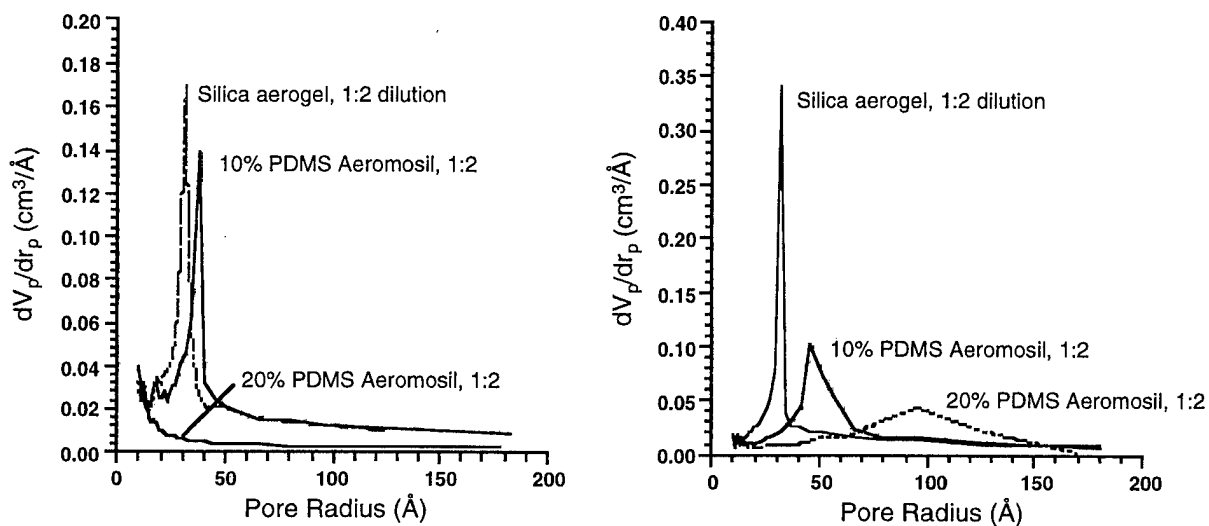
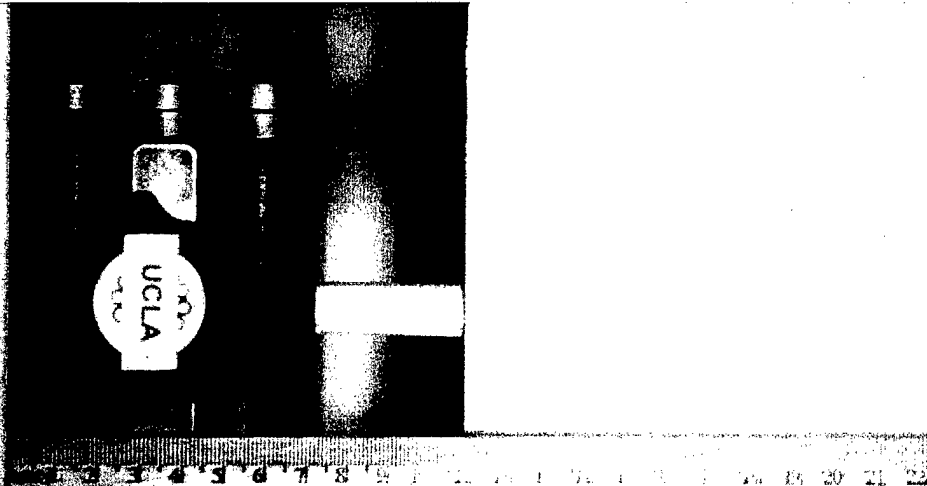
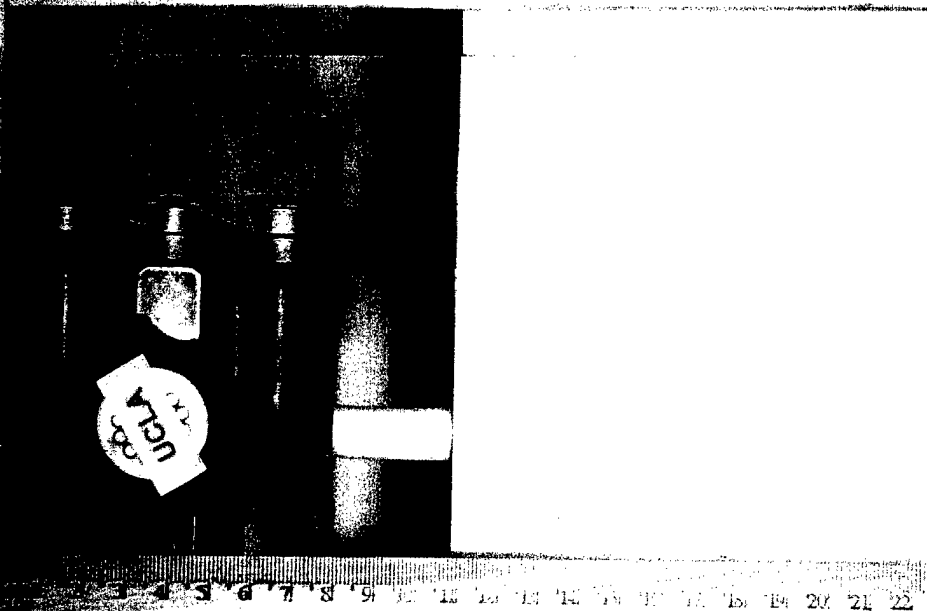


Figure 15 Pore size distributions for aerogels with varying concentrations of PDMS, a) acid catalyzed and b) acid/base catalyzed

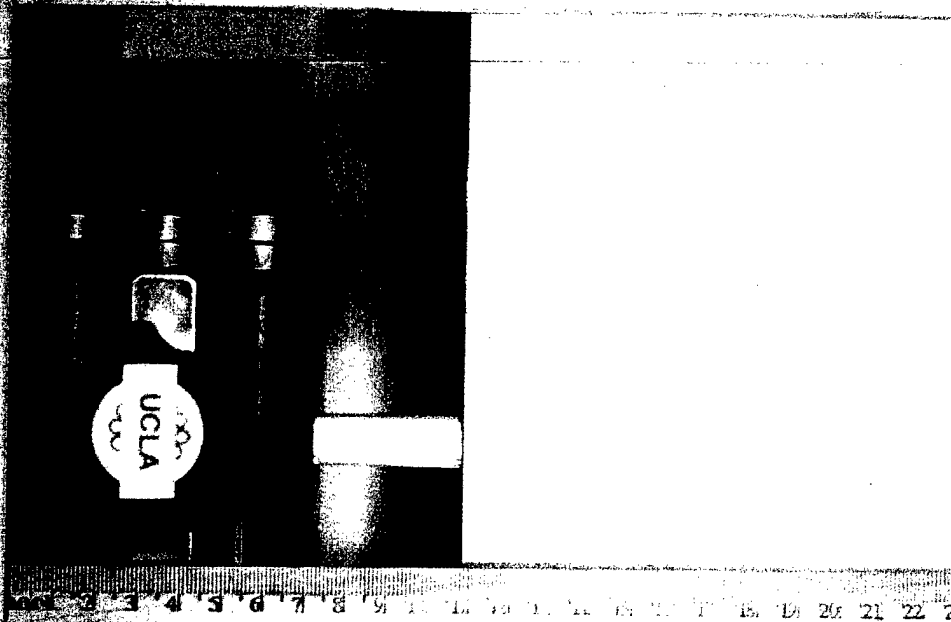
Figure 16 Rubbery Behavior of Aeromossils



Materials Science



Materials Science



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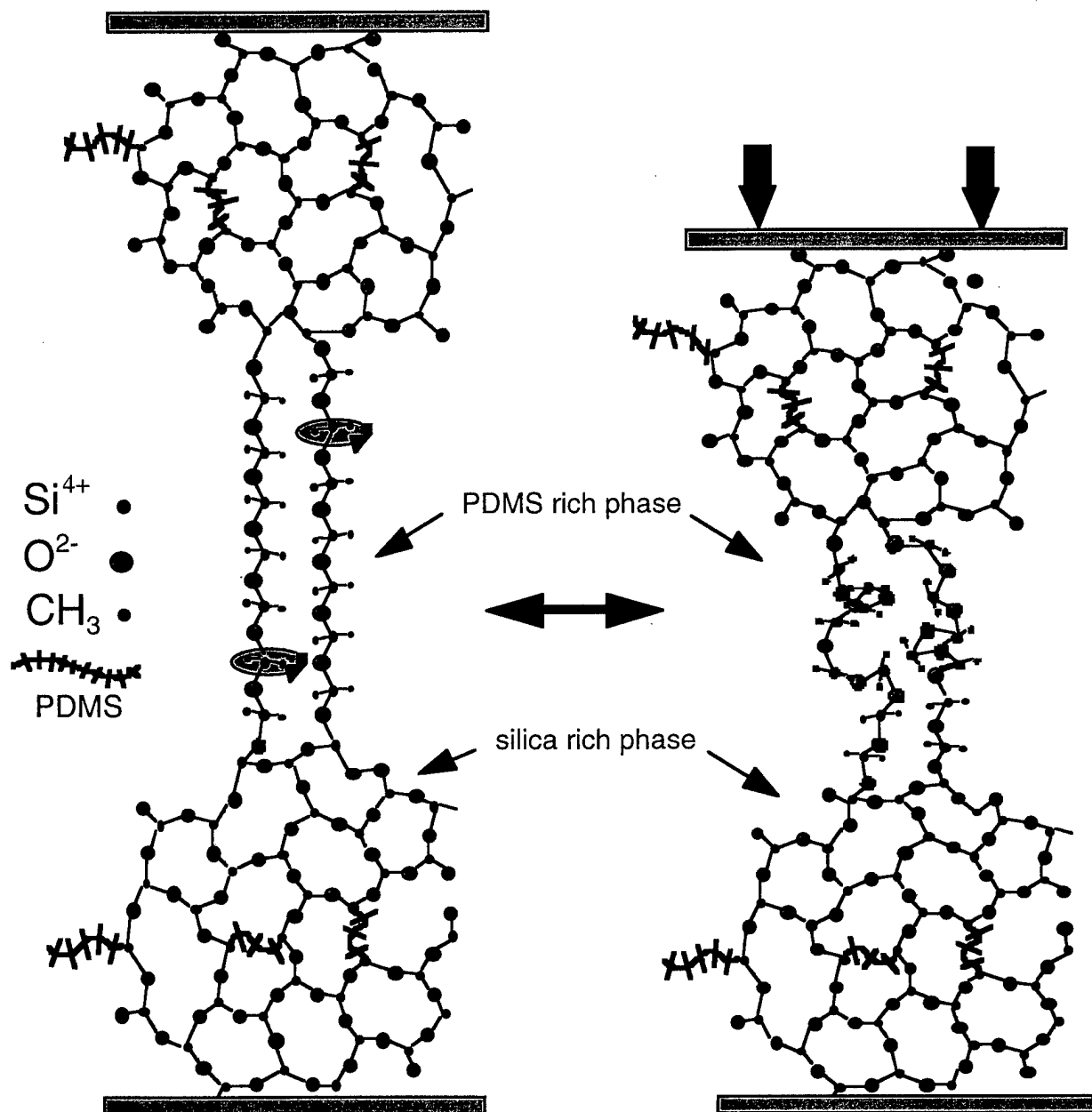


Figure 17 Model of rubbery behavior in Aeromosils based on preferential phase segregation of PDMS and silica rich phases

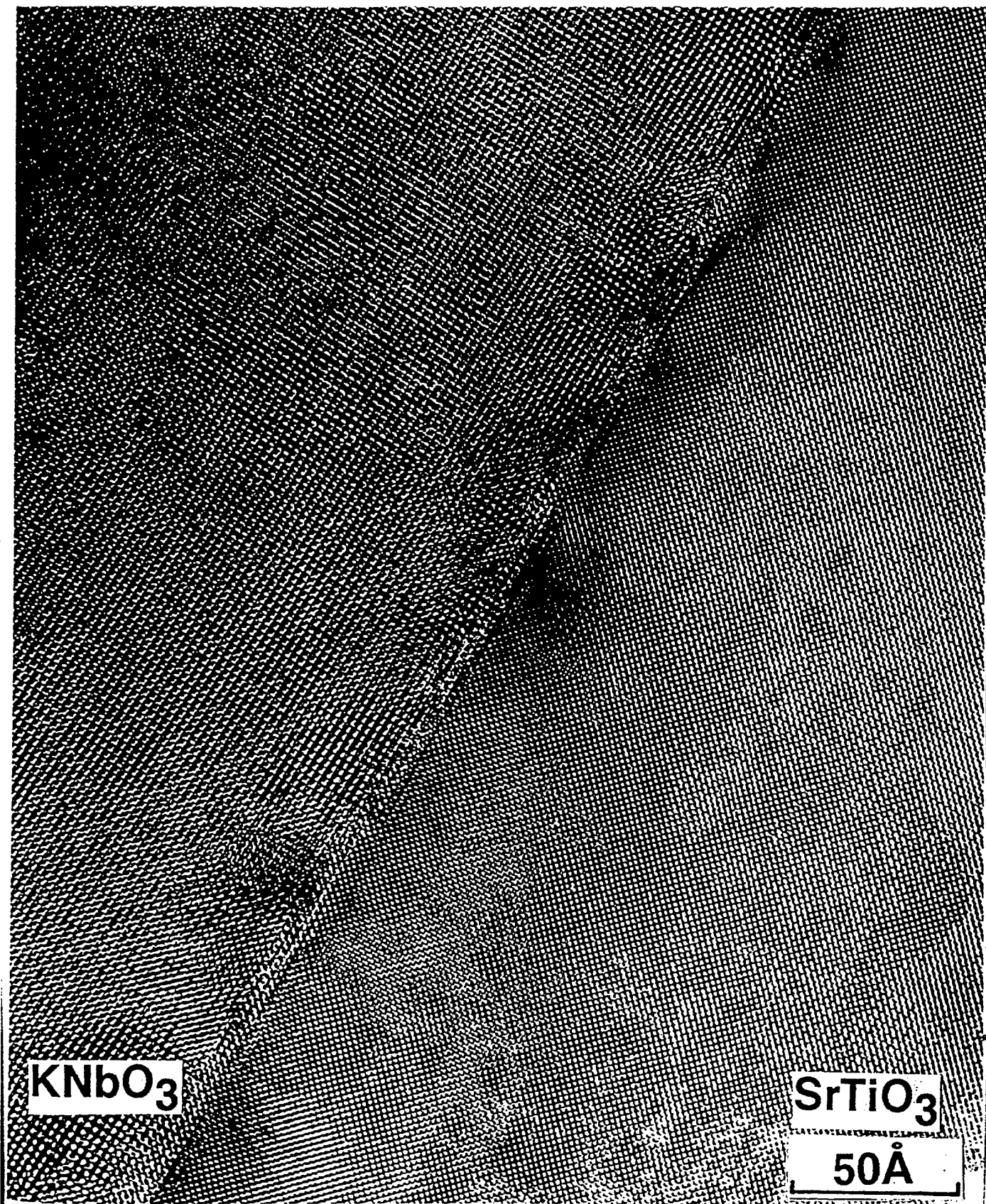
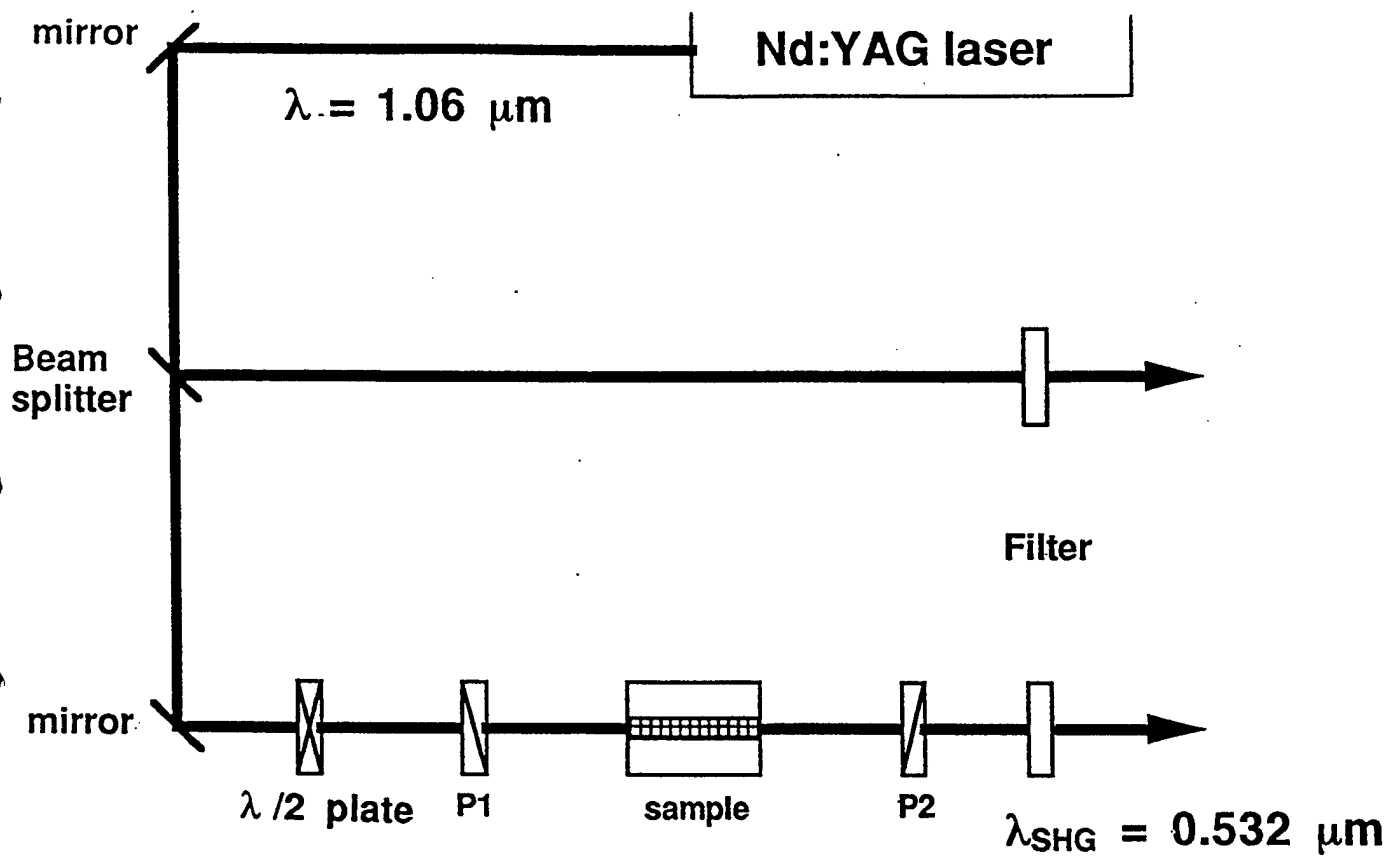


Figure 18 Lattice fringe image of epitaxial single crystal  $\text{KNbO}_3$  film on  $\text{SrTiO}_3$





waveguide of  $\text{KNbO}_3$  thin film

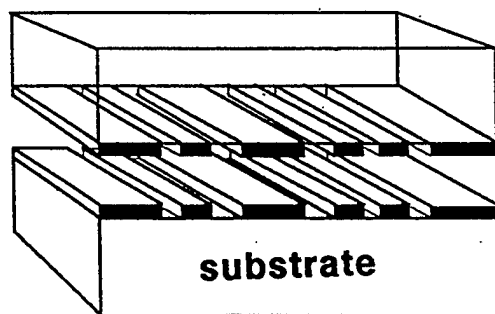
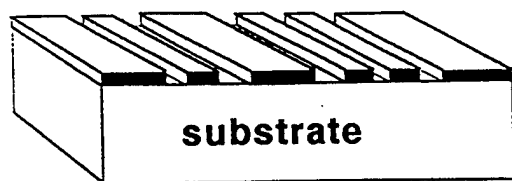


Figure 19 The experimental setup for the second harmonic generation and the waveguide pattern of the epitaxial  $\text{KNbO}_3$  thin films

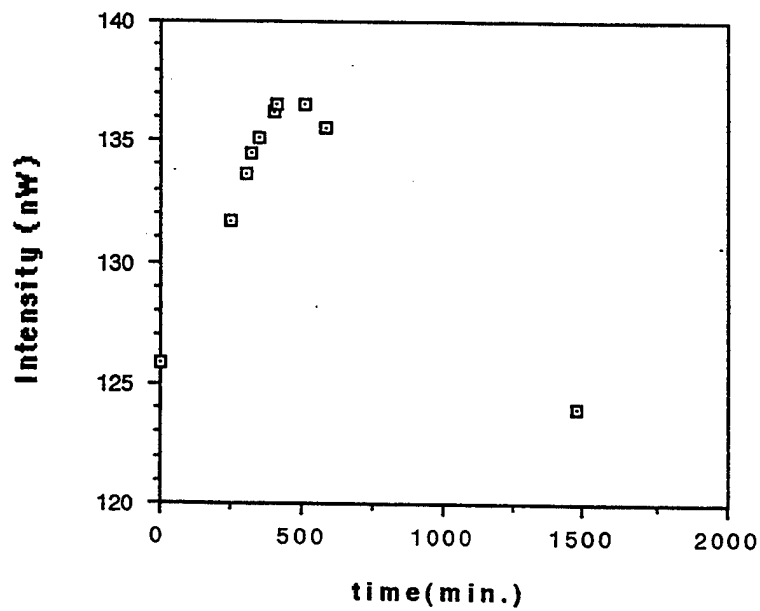
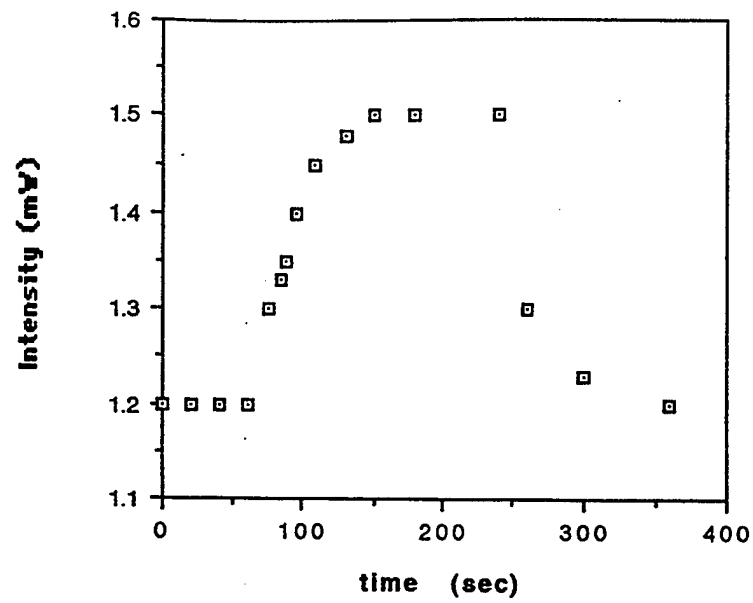


Figure 20 Intensity amplification of the laser light by using (a)  $\lambda = 0.532 \mu\text{m}$ , 1.2 W, (b)  $\lambda = 0.633 \mu\text{m}$ , 0.3 mW, in the Fe-doped  $\text{KNbO}_3$  thin films by the two-wave mixing experiments

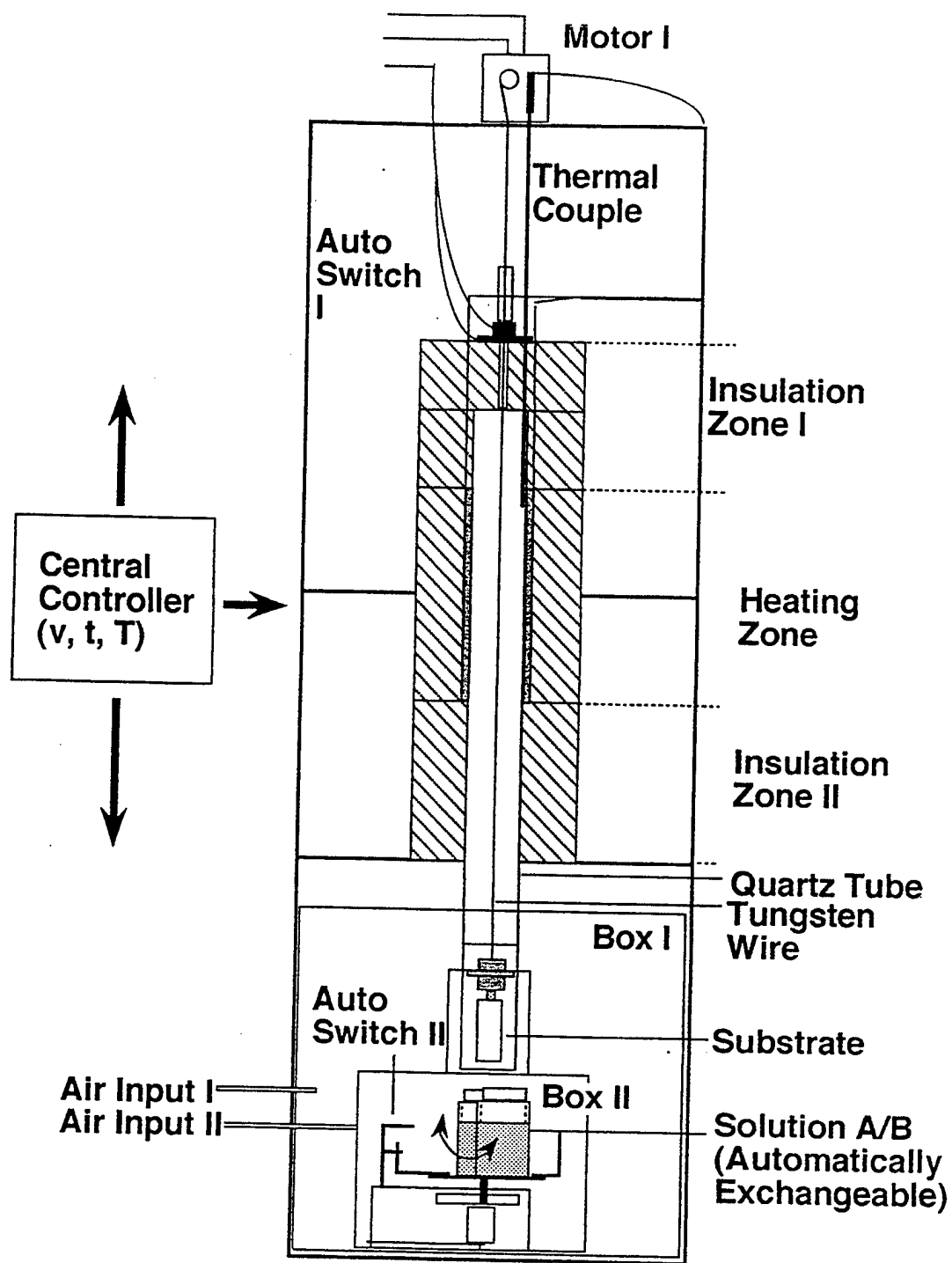


Figure 21 Schematic drawing of the automatic dip-coating and heating apparatus

## SEM CHARACTERIZATION

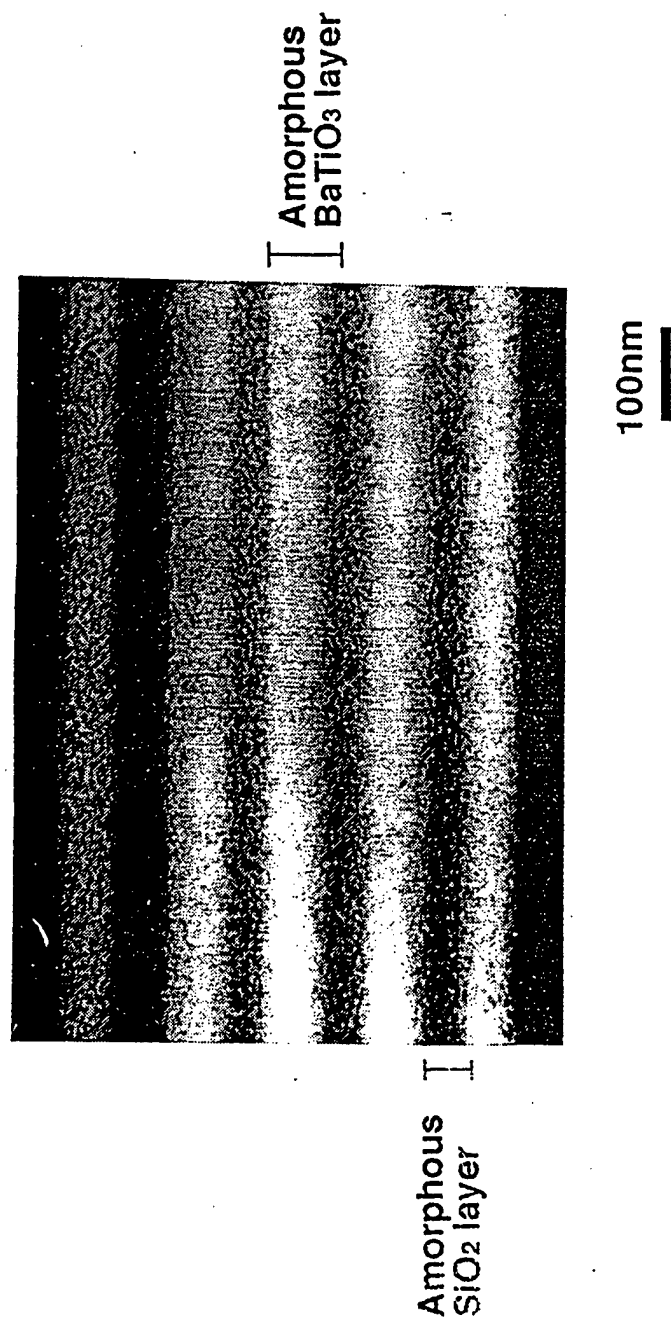
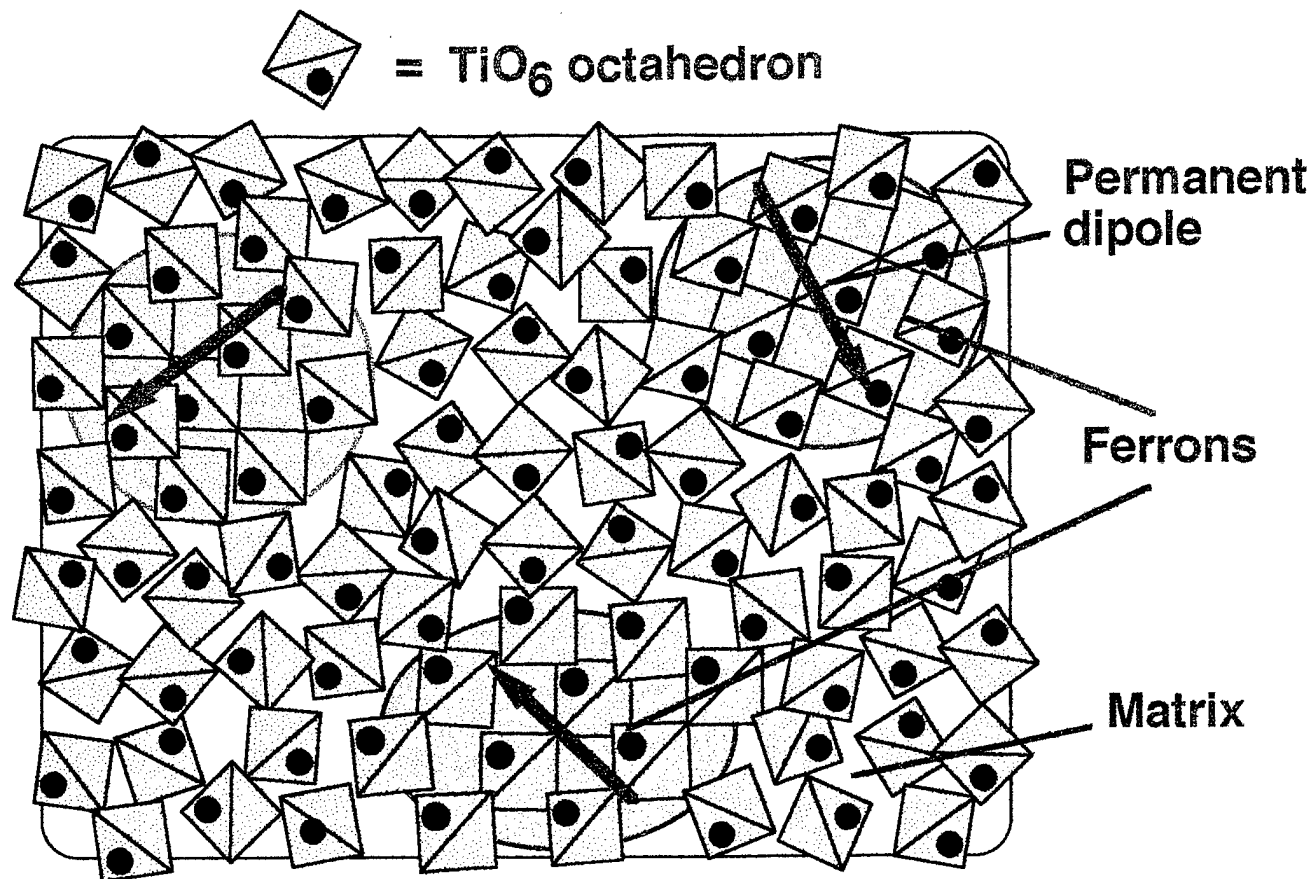
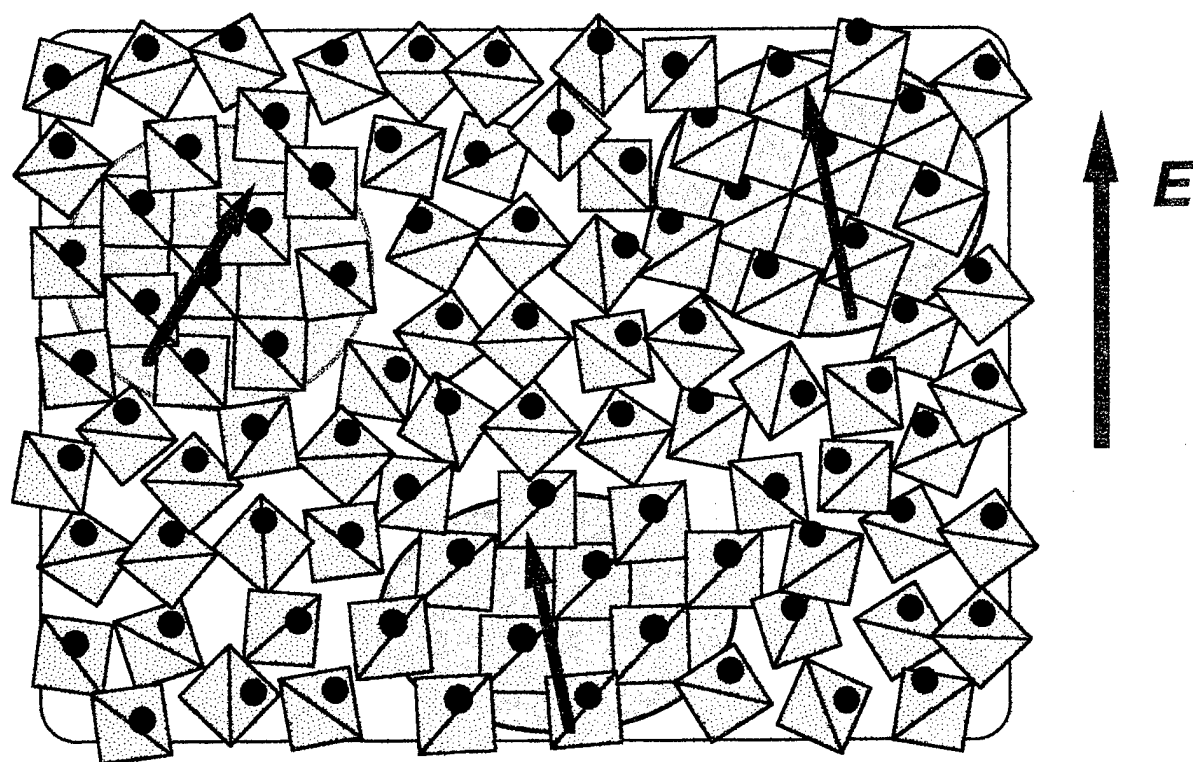


Figure 22 Electron micrograph of the cross-section through layers of amorphous  $\text{BaTiO}_3/\text{SiO}_2$  films, where dark layers represent  $\text{SiO}_2$  and white layers represent  $\text{BaTiO}_3$  (deposited alternately from solutions of 0.25 M  $\text{BaTi(OR)}_x$  and 0.87 M  $\text{Si(OC}_2\text{H}_5)_x$  upon fused silica substrates and fires at 400 °C



(a) Before poling



(b) Poling by Field  $E$

Figure 23 The "ferron" coupling model for oxide ferroelectrics

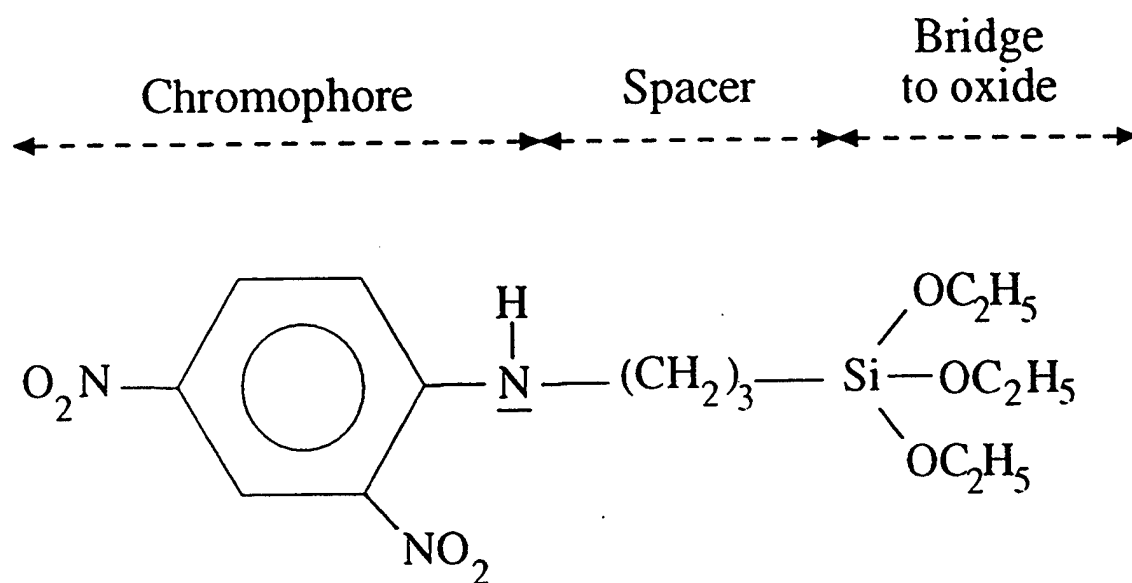


Figure 24 TDP: Triethoxy-silyldinitro-phenylamine

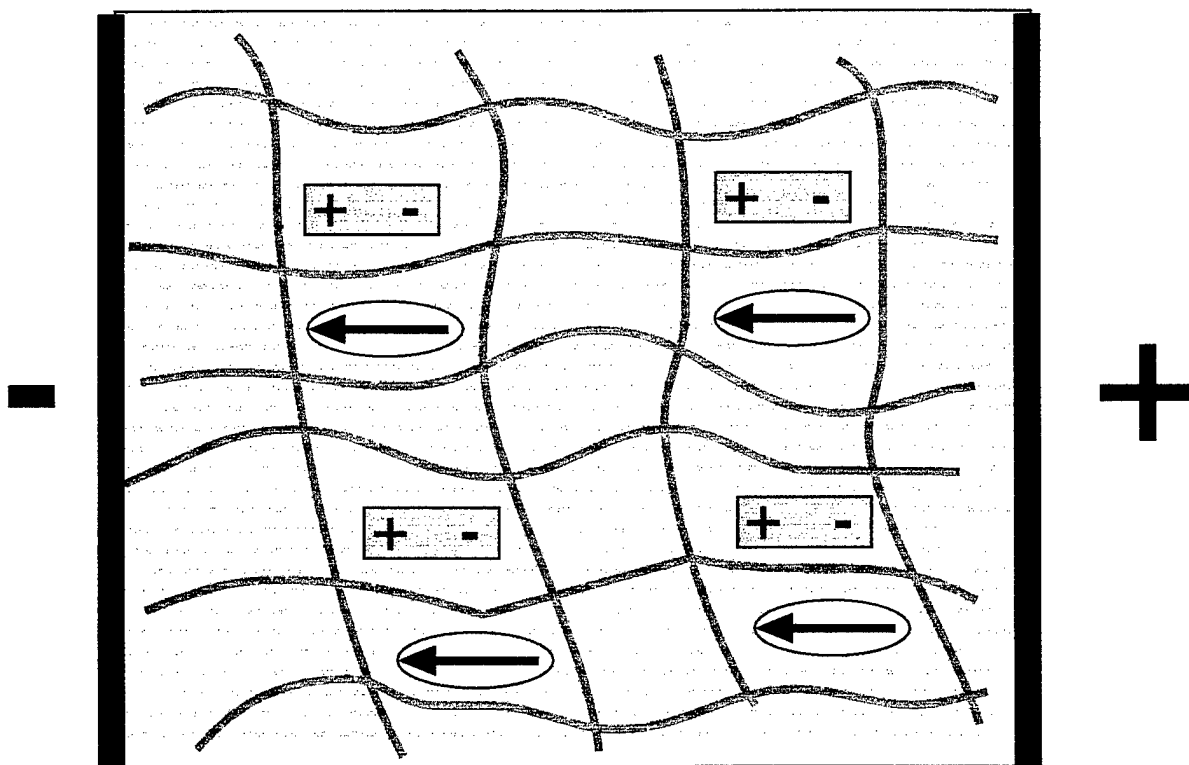
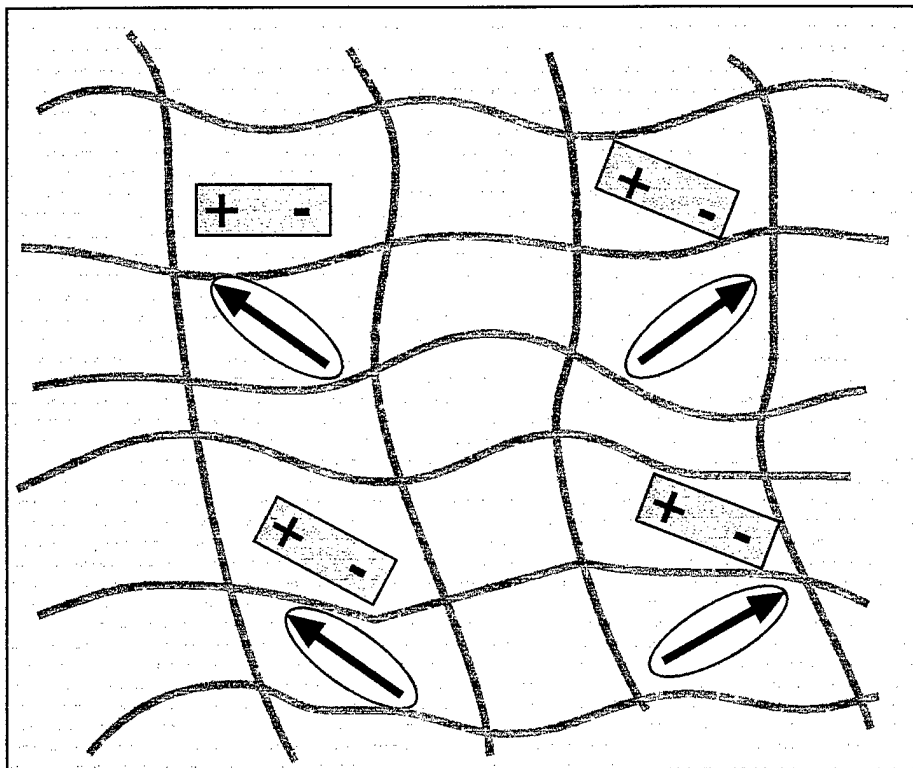


Figure 25 Electrical interactions of organic groups (arrow) and inorganic groups (+ -) in a gel matrix



**45 mol% TDP-45 mol% LiNbO<sub>3</sub>-10mol% TEOS film**  
**200°C/ 2hr**

**Figure 26 P-E Hysteresis loop in gel film**





200° C/2hrs

Figure 27 Ferron in 45 TDP-45  $\text{LiNbO}_3$ -10  $\text{SiO}_2$

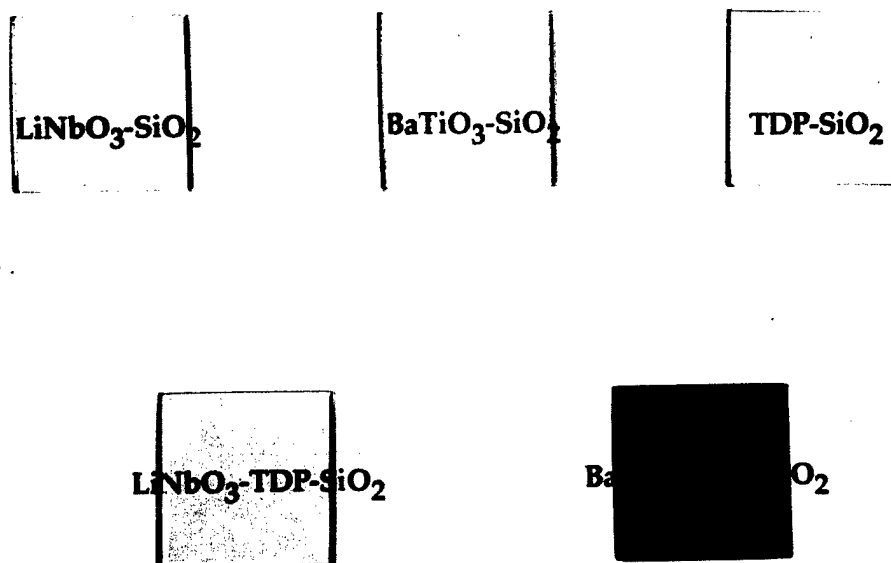


Figure 28 Organic-Inorganic Hybrid Films